CHEMICAL CHARACTERISATION OF NUCLEAR MATERIALS FOR TRACE ELEMENTS

By

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DEDICATIONS

I dedicate this dissertation to

My beloved uncle (Pedananna),

Late. Shri. P. Kasi Visweswararao

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CONTENTS

Synopsis

The increasing awareness of the important role of very small amounts of elements in chemical, physical and biological systems has greatly stimulated the refinement and extension of analysis at these levels. The analytical requirements imposed by the minute quantities and typically complex matrices involved have led to the development of methodologies and instrumentation so specialized as to warrant consideration as a distinct field of analytical chemistry - trace analysis. The meaning of trace is considered as a constituent making up only a small portion of the sample, the upper limit of the trace being about 100 parts per million by weight.

In front-end nuclear fuel cycle activities, chemical characterization of nuclear fuels and other reactor and structural materials for trace elements is indispensable. The performance of nuclear fuels in nuclear reactors critically depends on the presence of elements with high thermal neutron absorption cross sections as their presence is detrimental to the continued operation of the reactor. For example, nuclear fuels and other materials shall have to be characterised with respect to boron and very stringent specifications are laid down for boron in nuclear and other reactor structural materials such as Zircaloy. While boron presence is detrimental in some cases as mentioned above, it is also used for controlling the excess reactivity for safe operation of the reactor. Boron doped zirconium and Zr alloys are used for this purpose. An accurate knowledge of boron content with its associated uncertainty is absolutely required for the reactivity calculations. In the back-end cycle, the radioactive waste generated contains host of radionuclides produced in nuclear fission may have environmental concerns. The fission product ^{137}Cs has long half life (~ 30 years) and even if it is present in trace level in nuclear waste solutions, it has to be removed or separated from waste solution prior to safe disposal of the waste. A reliable analytical method is necessary for the determination of Cs in the waste being disposed.

A number of analytical methodologies do exist for the determination of trace elements such as boron and cesium. But there is still enough scope either for modification of existing methodologies or development of new ones. Even though, instrumental techniques like DC arc AES, ICP-AES and AAS are sensitive, possess multi-elemental analysis capability and are deemed to be workhorses for this purpose, they require matrix matched reference materials for the validation of results. Many times, matrix matched standards may not be available or are not accessible. In such cases, it is essential that the analytical measurements are validated by more than one technique based on independent principles. Moreover, boron being a critical trace constituent it is desirable to have the measurement carried out with as much high precision and accuracy as possible identifying all the possible sources of uncertainties to arrive at statistically acceptable expanded uncertainty in its measurement. With the multi-elemental techniques mentioned above, desirable precision achievable may not be achievable. Hence, there is a definite scope for developing alternative methodologies for the determination of boron from various nuclear materials.

In nuclear waste management, ^{137}Cs, one of the most abundant fission products, is a major radionuclide responsible for MANREM problems. Due to the toxicity of cesium and its ability to displace potassium from muscles and red cells, removal of cesium from medium and low level nuclear wastes also gained importance. Removal of ^{137}Cs from nuclear waste facilitates the safe and less expensive disposal methodologies, of high level waste in deep geological repositories as vitrified waste. Hence lot of research is going on to develop a suitable reagent or technique to remove effectively the Cs from nuclear waste. To asses the separation efficiency of a technique, Cs has to be determined. Radioactivity counting techniques based on gamma spectrometry offer very sensitive measurement option. However, obtaining radioactive Cs isotopes and its measurement may not be possible to all researchers. Also, determination of Cs with atomic absorption spectroscopy (AAS) involves expensive instrumentation and high cost of operation. It would be ideal to have a measurement technique which is reasonably sensitive, easily portable and at the same time can be applicable to measurement of stable cesium also. One approach that offers rapid, reliable measurements in aqueous environments is the polymeric membrane ion selective electrodes (ISEs).

Present investigations are therefore focused on (i) development of various methodologies to determine boron content present in various materials of interest in nuclear technology and (ii) development of ion selective electrode for cesium employing various calixarene compounds.

The thesis comprises five chapters.

The Chapter 1 describes introduction to trace analysis, a distinct part of analytical chemistry. It deals with the importance of trace analysis in nuclear industry; significance of analysis of boron in nuclear materials; various methodologies available for the determination of boron in nuclear materials; theoretical aspects of techniques namely Prompt Gamma Neutron Activation Analysis (PGNAA), spectrophotometry and ion selective electrode used in the present investigations. This chapter also describes various aspects of ion selective electrode methodology for calculation of mean ion activity and liquid junction potential.

Chapter 2 deals with development of methodology to determine low levels of boron employing chemical prompt gamma neutron activation analysis (PGNAA) at low neutron fluxes (10^6 n/cm^2/sec). Chapter 3 deals with the development and modifications wherever required, of methodologies for the determination of boron by spectrophotometry in various nuclear materials like U-metal, ammonium diuranate, uranium peroxide, uranium-aluminum-silicon inter-metallic compound and zirconium niobium alloy. It also dwells on the estimation of combined and expanded uncertainty arising in the measurements. Chapter 4 deals with optimization of different experimental conditions for determination of boron in zirconium niobium alloy samples by tetrafluoroborate ion selective electrode method. This chapter also describes the statistical treatment of the results obtained. Chapter 5 deals with development of ion selective electrode for cesium employing various calixarenes as an ionophore. Description about optimization of various parameters like membrane composition, inner filling solution composition is also given in this chapter. This chapter also deals with determination of cesium in simulated high level nuclear active waste employing developed ion selective electrode.

Chapter 1

(Introduction)

This chapter is divided into three parts. In the first part the concept of trace analysis is introduced. A brief mention of desirability of having a clean technology like nuclear energy for energy security is also made. In the second, analytical methodologies for boron determination are described. In the concluding part, the necessity of determining ^{137}Cs is mentioned.

The term “trace analysis” is extensively used to describe the application of analytical chemistry where amount of analyte is very small (a few micrograms). High purity material production is very important in diverse fields. One of the applications of these high purity materials is in preparation of high reliable electronic goods. Trace elemental analysis is one of the important requirements in the preparation/production of high pure materials. Trace elemental analysis is also essential to assess the quality of food products and to monitor the environmental contaminants.

Nuclear energy plays an important role in providing energy security and also as a means to resolve global warming issues. It is a clean and environmental friendly source of energy. It has the potential to meet the demands of energy for the coming few hundred years. Chemical quality control with respect to specification analysis of impurity content in nuclear fuels before they are loaded into nuclear reactor is one of the indispensable components. To characterize these materials, trace analysis plays key role.

Boron for the reasons mentioned earlier is a critical element requiring accurate determination. Natural boron contains about 20% of ^{10}B isotope, which has thermal neutron absorption cross-section (σ) of 3846 barns for the reaction ^{10}B (n,α) ^{7}Li, due to which lot of gaseous (helium) product is formed. This reaction (i) affects the neutron economy because of high σ and (ii) may lead to structural changes or cause damage to reactor materials due to release of gaseous product. The most commonly used techniques in nuclear industry are Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and DC arc Atomic Emission Spectroscopy. Obtaining reliable data from these techniques requires matrix matched reference material over the entire range of interest. Many times either they are not available or are not accessible. It is desirable to look for alternate methods in which the requirement of matrix-matched reference materials is not that critical.

Prompt Gamma Neutron Activation Analysis (PGNAA) is one of the sensitive methods to determine boron in various matrices. The principle of PGNAA of boron is measurement of characteristic gamma rays, which follow the absorption of thermal neutrons by the reaction ^{10}B (n, α) ^{7}Li. Most of the ^{7}Li (93%) produced is in excited state which decays within 5×10^{-14} s by emitting a 478 KeV gamma ray. Since the gamma ray is emitted while the recoiling ^{7}Li nucleus is in flight, it is Doppler- broadened. Even though PGNAA is non destructive technique, separation of matrix is essential to determine boron content in nuclear materials like uranium compounds. Additionally, at extremely low concentrations of boron, chemical separation and pre-concentration of boron (chemical PGNAA) is resorted to improve sensitivity in measurements. Also due to low neutron flux availability, large amount of uranium sample (10 g) required for each analysis. In the present investigations, to check the feasibility of Chemical PGNAA for determination of boron, ground water samples were selected. Solvent extraction with 2-ethyl hexane 1,3 diol employed for separation and pre-concentration of boron. This chapter describes PGNAA technique and Compton suppressed gamma spectrometry and also fundamental aspects of solvent extraction.

A simple instrumental technique like spectrophotometry is a better option for determination of boron in nuclear materials as it does not require matrix-matched reference materials. At the same time, it is also possible to get same extent of sensitivity as in ICP-AES and DC arc-AES by choosing a suitable chromogenic reagent. Various reagents are used as complexing reagents for determination of boron in diverse matrices. The most commonly used reagent is curcumin because of its high sensitivity and stability with boron. Even though it is sensitive for boron determination, to overcome the interference from other elements, separation of boron is required before colour development. Solvent extraction is usually preferred to separate boron. As the aim of present studies is to determine boron content in various precious materials with minimum sample size, check the reliability of the methodology by studying effect various impurities and reagents and estimation of uncertainty associated with the methodology to increase the confidence on measurement values, the existing methodologies for the determination of boron in nuclear material have to be appropriately modified. The present chapter also describes briefly about instrumentation of spectrophotometer.

Due to long half life and high thermal output, ^{137}Cs is one of the fission products of concern to environmentalists for safe disposal of radioactive nuclear waste streams. A lot of research is going on around the world for removal of cesium from waste solutions. For quantitative separation of Cs, various macrocyclic compounds and inorganic complexing agents are being developed. To determine the separation efficiency of these reagents, there is a need to develop a simple measuring technique like ion selective electrodes. With this in view, the present studies have been undertaken to develop an ion selective electrode for cesium employing various calixarenes. The aim of the present investigation is not only to charactarise the developed ISE for properties like sensitivity, selectivity, response time and lifetime also application of ISE to determine Cs in simulated nuclear waste and to determine loading capacity of polymerized beads. The present chapter also gives details of instrumentation involved in ion selective electrode and working principle of reference electrodes.

Chapter 2

Determination of boron by Chemical PGNAA

PGNAA is one of the sensitive and non-destructive methods for determining boron. Uranium undergoes fission during irradiation with neutron beam and emits almost entire range of energy of gamma rays. Hence, to determine boron in uranium compounds, it has to be separated from the matrix before analysis. In the research reactor DHRUVA, the available neutron flux at sample holder of PGNAA setup is only 1.0×10^6 n/cm^2/Sec. Hence, to determine boron content in uranium compounds at the level of 0.5 μg/g, we require about 10 g sample. With a view to reducing the sample amount requirements, pre-concentration of boron from a small sample size of uranium prior to PGNAA was thought off.

For checking the feasibility of the method, boron content was determined in groundwater samples collected from Khuchch, Gujarat, India after selective separation and pre-concentration of boron using 2-ethylheaxane 1,3 diol (EHD). In this methodology, about 10-15 g of water sample was aliquoted and acidified with 6M HCl. Boron was selectively extracted with 10% EHD in chloroform employing batch extraction. From the separated organic phase, $CHCl_3$ was evaporated. The residue leftover after evaporation of $CHCl_3$ was transferred to a Teflon sample holder of PGNAA set-up with the help of N, N Dimethylformamide. Prompt gamma spectra are acquired online while the sample is under irradiation. Intensity of Doppler broadened peak of 478 keV was measured. The calibration plot was plotted between amount of boron present in aliquot and intensity of gamma ray by analyzing standard boric acid samples containing 30-150 μg. The sensitivity of 18.8 cps/mg-B is obtained from the slope of calibration plot. Detection limit of the method is 0.3 μg/g when counted for 35,000 seconds for sample size of 10 gram. The analytical results of present method agreed well with well-established spectrophotometric determination of boron as boron - curcumin complex and ICP-AES. The present method has an added advantage that, all the interfering elements in PGNAA of B have been eliminated. Employing the present method, boron in nuclear grade uranium compounds can be determined if the high neutron flux (10^8 n/cm^2/sec) is available, wherein matrix separation is necessary for PGNAA determination of boron.

Chapter 3

Determination of boron by spectrophotometry

Part I: determination of boron in uranium compounds

Detailed investigations have been carried out on the well-known method of spectrophotometric determination of boron particularly in uranium compounds as boron–curcumin complex after extraction into 2-ethyl hexane 1,3-diol (EHD) to understand a number of parameters, which have not been addressed earlier in the literature. Effect of different acid media like HCl, HNO_3, H_2SO_4 and H_3PO_4, which are employed for dissolution of nuclear fuel samples, on analytical results of boron has been one such parameter. It was found that HNO_3 significantly interferes in boron determination. Detailed studies are carried out to investigate the cause for interference and its elimination. The interference from HNO_3 is eliminated by leaching of extracted HNO_3 with 0.5 M HCl. Between the diluents namely ethyl alcohol and N,N-dimethyl formamide (N,N DMF) which are employed for final dilution on sensitivity of method, N,N DMF is ideal at lower dilutions. Studies have also been carried out to find out the loss of boron, if any, during conversion of uranium compounds to U_3O_8. Based on the present studies, the existing procedure has been suitably modified to improve the sensitivity in the measurements. In addition, possible interference of Al, Cr, Mg, Ca, Fe, Mn, Mo, F- and W (which are usually present in the sample) and amount of EHD in boron determination was investigated. There was no interference from these elements even when they are present at 1000 times of boron content. Absolute detection limit was found to be 10 ng. The precision and accuracy of the method is 3% at level 100 $ng.g^{-1}$ of boron.

Part II: Determination of boron in uranium aluminum silicon inter metallic compounds

A simple and sensitive method has been developed for the determination of boron in Uranium-Aluminum-Silicon alloy based on leaching of boron from the sample by treating with 6M HCl and H_2O_2, its selective separation by solvent extraction with EHD and quantification by spectrophotometry using curcumin. The method has been evaluated by standard addition method and validated with an independent method based on dissolution of sample by acid digestion and determination of boron by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Relative standard deviation (precision at 1 σ level) of the method is 3.0%. Boron concentration has been determined in U-Ai-Si alloy samples without using hydrofluoric acid and nitric acid. Boron content has been determined at levels less than 0.5 $\mu g\ g^{-1}$, in 200 mg sample (quantification limit of the method is 0.2 $\mu g\ g^{-1}$). This method has been extended to determine boron in various silicon related materials of interest in nuclear technology like SILUMIN, Si-Al alloy and U_3Si_2.

Part III: Determination of boron in Zirconium – Niobium alloys

The methodologies available in the literature are mainly meant for zircaloy samples. The same method could not be adopted for Zr-Nb samples, necessitating the development/modification of the dissolution procedure and determination of boron. In this methodology, sample was dissolved in $(NH_4)_2SO_4$ and H_2SO_4 in round bottomed flask fitted with water cooled condenser, without the loss of boron. After dilution of solution suitably, an aliquot of solution was taken and boron was determined as mentioned earlier. The method has been evaluated by standard addition method and validated by ICP-AES method. The present method significantly improves the accuracy and precision over the reported methodologies.

Part IV: Estimation of uncertainty in spectrophotometric method

Since no matrix matched certified reference material for boron is available, in the present studies, "bottom-up" procedure, which uses each component of the quantification formula of measurand, was employed to evaluate the total uncertainty of measurement. These include sample preparation such as solid aliquoting from the sample, chemical treatment, absorbance measurement of test portion, evaluation of the measurement, quantification of the analyte along with associated uncertainty. All possible sources of uncertainties in the methodology (both Type "A" and type "B") have been individually assessed, following the "Guide to the Expression of Uncertainty in Measurement" published by the International Organisation for Standardisation (ISO). After converting each uncertainty component (u_i) to relative standard uncertainty and then combined uncertainty (u_c) was calculated employing uncertainty propagation formulae. Depending on the matrix and content of boron expected, different solid aliquots were taken for analysis. The combined uncertainty in spectrophometric determination of boron in uranium compounds is 4.4% and in zirconium - niobium alloy it is 4.7%. Therefore, expanded uncertainty is 8.8% and 9.1% respectively for uranium compounds and zirconium-Niobium alloy samples at 95% confidence level.

Chapter 4

Determination of Boron in Zr-Nb Alloy Samples by BF_4^- Ion Selective Electrode

Even though spectrophotometric determination of boron is sensitive and accurate, the method adopted is time consuming. A need therefore existed for a simple and fast methodology to determine boron content in zirconium samples on routine basis. In view of the refractory nature of the alloy, boron determination in these type matrices is a challenging task for analytical chemists. Also due to non-availability of matrix matched reference materials, direct solid analysis cannot be resorted to. With this in view, a simple and sensitive method based on potentiometric determination of boron as tetrafluoroborate with tetrafluoroborate ion selective electrode has been developed. After dissolving the sample, boron was quantitatively converted to BF_4^- with HF. Potential response in the solution was measured with Orion 9305 BN BF_4^- ion selective electrode. The response of the ion selective electrode was Nernestian in the range of 0.1 to 100 µg/mL of boron in the solution. The method has been validated by two independent methods namely spectrophotometry and Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES). Precision and accuracy of the method is 3.7% and 3.0% respectively. All possible sources of uncertainties in the methodology have been individually assessed. The combined uncertainty is calculated employing uncertainty propagation formulae. The expanded uncertainty in the measurement at 95 % confidence level (coverage factor 2) is 6.3%.

Chapter 5

Development of ion selective electrode for cesium

Cesium is one of the important fission products. Its activity or concentration has to be measured in all types of nuclear wastes. In recent days ion selective electrode technique gained importance as analytical tool because of its simplicity, ruggedness and fastness. Many of the Cs-selective ISEs available or reported in literature have limited lifetime of maximum of a four months only. One of the aims of present investigation is to fabricate an ISE for Cs with a reasonably long life. With this in view, studies are carried out to develop ISE for cesium employing different calixarene compounds.

Part I: Cs ISE with Azocompound

A polyvinylchloride (PVC) based liquid membrane Ion Selective Electrode (ISE) for cesium was fabricated with 5-(4′-nitrophenylazo) 25,27-bis(2-propyloxy)26,28-dihydroxycalix[4]arene as ionophore. It is well known that membrane constituents also play key role in response of ISE. Hence different membrane constituents were investigated to realise optimum performance of the ISE developed. Of the four plasticizers and two ion additives studied, the best response was observed with membrane having 2- nitro phenyl octyl ether (oNPOE) as plasticizer and potassium tetrakis (perchloro phenyl) borate (KTpClPB) as an ion additive. Effect of concentration of inner filling solution was also studied and found that 10^{-1} M CsCl as inner filling solution gave better response for Cs. The optimised ISE gave response over concentration range of 10^{-5} to 10^{-1}M CsCl. The near Nernestian slope of the response was 56 mV per decade for Cs with a response time less than 20 seconds. Matched potential method (MPM) has been applied to find out the selectivity for Cs over several ions like Rb^+, K^+, Na^+, NH_4^+, Sr^{+2}, Ba^{+2}, Ca^{+2}, Mg^{+2}, Cu^{+2}, Pb^{+2}, Zn^{+2}, Ni^{+2} and Ce^{+3}. The response of ISE for Cs^+ was fairly constant over the pH range of 3 to 11. The lifetime of the electrode is 9 months which is the highest life for any membrane based Cs - ISE so far developed. The concentration of cesium in two simulated high level active waste streams was determined and results agreed well with those obtained independently employing Atomic Absorption Spectrometry.

Part II: Cs ISE with calix[4]arene crown-6 compounds

Studies were carried out to develop liquid membrane based ion selective electrode for cesium with three compounds namely, dioctyloxycalix[4]arene crown 6 ether (DOC4C6), calix[4]arenecrown 6 ether (C4C6) and dimethoxycalix[4]arene crown 6 ether (DOMC4C6). The best response was observed with DOC4C6. Different membrane constituents were investigated to realise optimum performance of the ISE developed and the best response was observed with membrane having 2- nitro phenyl octyl ether (oNPOE) as plasticizer and potassium tetrakis (perchloro phenyl) borate (KTpClPB) as ion additive.

The main limitation of conventional ion selective electrode is detection limit which are in the range of micromolar concentration range. This limitation was found to be due to use of high concentration of primary ion in inner filling solution, which is essential for maintaining constant activity of primary ion. To achieve lower detection limits, maintaining of low concentration of Cs in inner filling solution is essential. To maintain the low and constant activity of primary ion in inner filling solutions either chelating agents or ion exchange resin could be used. Since water soluble chelating agent for cesium is not available, Dowex 50w 1X8 ion exchange resin was used to maintain low concentration of primary ion (Cs) and high concentration of interfering ion (Na). Nernstian response was observed over concentration range of 10^{-6} to 10^{-1}M CsCl with detection limit of 2.1×10^{-7} M Cs. The slope of the response was 57 mV per decade for Cs with a response time less than 10 seconds. Separate solution method (SSM) has been applied to find out the selectivity for Cs over several ions like Rb^+, K^+, Na^+, NH_4^+, Sr^{+2}, Ba^{+2}, Ca^{+2}, Mg^{+2}, Cu^{+2}, Pb^{+2}, Zn^{+2} and Ni^{+2}. One advantage of developed ISE is the selectivity of Cs over sodium with log $K_{Cs/Na}$ of -4.56. Hence it could be used to determine Cs in nuclear waste solution where low concentration of Cs has to be determined in presence of high concentration of Na. Life time of ISE is 10 months. This is the longest life for any Cs ISE so far reported.

The developed ISE is used to determine Cs concentration in two simulated nuclear waste solutions by standard addition and dilution method. Results agreed well with AAS method. The present ISE is also employed to determine Cs loading capacity of inorganic ion exchange material polymerized as polymeric beads.

Summary and Highlights of the present work

1. Using low neutron fluxes, about 10^6 n/cm^2/Sec, boron in ppm levels was determined employing Chemical PGNAA. This is the first time chemical PGNAA has been employed to determine boron.

2. The well known spectrophotometric method for the determination of boron in uranium compounds with curcumin after extraction with 2-ethyl hexane 1,3 diol has been modified such that the sample size is reduced from 2.5g to 0.200g. Extensive investigations have been carried out to study the reasons for nitric acid interference in methodology and to circumvent the same. These studies are essential in nuclear technology since different acids are employed to dissolve uranium compounds.

3. To our best of knowledge, first time spectrophotometric method has been developed and employed for the determination of boron in uranium-aluminum-silicon inter metallic compound. This method has been extended to determine boron in various silicon related materials of interest in nuclear technology like SILUMIN, Al-Si alloy and U_3Si_2.

4. Spectrophotometric method employing curcumin has been modified for the determination of boron in highly refractory material Zr-Nb alloy. Dissolution procedure has been modified suitably to prevent the loss of boron. Due to selective separation of boron with 2-ethyl hexane 1,3 diol, reported interference from tin was avoided and also precision and accuracy has been improved considerably compared with literature reports.

5. To increase the confidence on measurand values, uncertainty in spectrophotometric method for the determination of boron was estimated by following ISO guidelines.

6. A simple and sensitive method for the determination of boron in Zr- Nb alloy samples based on commercially available BF_4^- ISE has been developed. Conditions are optimized to determine boron with BF_4^- ISE in zirconium matrix which is forming highly stable complex with fluoride ion. This is the first time to determine boron in Zr-Nb alloy samples employing BF_4^-. To increase the confidence on measured values combined and then expanded uncertainty the methodology was estimated.

7. New ion selective electrode for cesium was developed employing 5-(4′-nitrophenylazo) 25, 27-bis(2-propyloxy)26,28-dihydroxycalix[4]arene as an ionophore . Developed ISE is having good selectivity for Cs over Na which is essential for determination of Cs in nuclear waste solutions. One of the advantages of the developed ISE is having life of nine months.

8. Various calix[4]arene crown -6 compounds are tested for preparation of Cs ISE and best response was observed with dioctyloxycalix[4]arene crown 6 . Employing ion exchange resins in inner filling solutions, response and selectivity for cesium are improved. Employing developed ISE, Cs concentration in simulated high level nuclear waste solutions was determined employing standard addition and dilution method. The loading capacity of polymeric beads for Cs as also determined. The life time of the electrode is 10 months which is longest life time so far reported for any Cs ISE.

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Chapter 1

Introduction

1.1. Trace analysis

The increasing awareness of the important role of very small amounts of elements in chemical, physical and biological systems has greatly stimulated the refinement and extension of analysis at these levels. The analytical requirements imposed by the minute quantities and typically complex matrices involved have led to the development of methodologies and instrumentation so specialized as to warrant consideration as a distinct field of analytical chemistry - trace analysis. In the beginning of the 19th century "trace" is defined as any element whose concentration in a certain medium is too low to be quantitatively determined. In gravimetric and volumetric analysis, it is still usual to designate all concentrations lower than the sensitivity limit of the analytical method as "traces" or "content too low to be determined". Due to advances in science and technology, the minimum detectable concentrations in a given medium keep decreasing. Consequently, the concentration levels formerly designated as "traces" now fall within the range of concentrations which can be determined by instrumental methods like spectroscopic methods, electrochemical methods and nuclear analytical methods. In general "trace analysis" refers to the determination of element of interest in any matrix which is containing less than 0.01 wt%. Depending on the content of element of interest in matrix, it is considered as major, minor, trace and ultra trace element. They are characterized as a following way

Major: >1 wt%
Minor: <1 wt% and >0.01wt%
Trace: <0.01wt% and >0.0001wt%
Ultra trace: <0.0001 wt%.

1.2. Importance of trace analysis

It is a well established fact that the physical properties of metals and alloys can be profoundly affected by extremely minute concentrations of certain elements. The list of metallurgical properties that are significantly altered (for good or otherwise) by residual level of elements is quite extensive. In most of the cases, these effects are deleterious. Residual elements in the major matrix may be due to the result of unwanted contamination from extraneous environment from materials that contact the product during processing or storage. There are also cases where, trace elements are known to cause beneficial effects and are intentionally added to alloys either for their own influence or for the synergistic influence they exert on the effects of other alloying additions. Nowadays trace analysis is one of the factors to improve the economy of a country. Trace analysis is required to characterise very pure materials that are essential to prepare good quality electronic goods. Also trace analysis is essential to assess the quality of food products and to monitor the environmental contaminants. Trace analysis also plays key role in chemical quality control of nuclear and reactor materials in nuclear technology.

1.3. Importance of nuclear technology in India

With the growth of industrial development and domestic requirements, there is need for a substantial increase in the energy production in India. In the coming decade, the installed capacity is required to be doubled from the present capacity of about 1,00,000 MWe. The conventional methods of power production are coal and hydel based. The environmental concerns and the substandard quality of Indian coal will not permit larger installed capacity of thermal plants. The hydel resources are limited to 35,000 MW capacity and involve environment and human resettlement problems. Presently non conventional energy resources like wind and solar energy are highly cost intensive as the cost per kW of power is too high to be economically viable.

Nuclear power is poised for a renaissance and is an inevitable option for a large developing country like India to meet the ever increasing demand of electricity, at an affordable cost to the common man and without degrading the environment in terms of global warming. 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 i.e., pressurized heavy water reactors, utilization of plutonium which is generated in first stage in second stage i.e. fast breeder reactors, for breeding of ^{233}U from ^{232}Th. Finally utilization ^{233}U in third stage as a fissile material along with thorium, uranium and plutonium in advanced heavy water reactors.

1.4. Importance of trace analysis in nuclear technology

In nuclear fuel cycle activities, in the front-end cycle, chemical characterization of nuclear fuels and other reactor and structural materials for trace elements is indispensable. The performance of nuclear fuels critically depends on the presence of elements with high thermal neutron absorption cross sections as their presence is detrimental to the continued operation. 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 and trace constituents which affect the fuel properties and hence its performance under conditions prevailing in an operating reactor.

Nuclear reactor design incorporates detailed specifications of different systems, which must be satisfied for smooth and efficient functioning of the reactor. Fuel being the heart of the reactor, its chemical characterisation is an important component of this design. Both the fuel materials and finished fuel products are to be characterised for this purpose. Each fuel batch has to be subjected to comprehensive chemical quality control for trace constituents, stoichiometry and isotopic composition. Presence of trace elements in nuclear materials affects the nuclear reactor operation significantly. This is mainly because of adverse changes in neutron economy, fuel integrity, thermal and mechanical properties and failure of clad occurring due to presence of some of the trace constituents. In order to attain reliable, safe and efficient nuclear reactor operation there is need to monitor and control the trace constituents in nuclear materials prior to their use. Hence control of trace constituents in the fuel is necessary to obtain the designed burn-up. Certain upper concentration limits have been specified for a number of trace elements in nuclear fuel materials. These are called specification limits. It is interesting to note that during the time of first nuclear reactor construction in USA in 1940's, designers, with whatever knowledge and expertise available with them at that time and in consultation with nuclear physicists, technologists and chemists laid down these specifications. It is remarkable that these specifications are accepted even today.

In particular, boron, which is having very high thermal neutron absorption cross section, has very stringent specification for all nuclear and reactor materials. Natural boron contains about 20% of ^{10}B. The thermal neutron absorption cross-section (σ) is 3846 barns for the reaction ^{10}B (n,α) ^{7}Li, due to which lot of gaseous (helium) product is formed. This reaction affects the (i) neutron economy and (ii) may lead to structural changes/damages to reactor materials. Hence, all the nuclear materials have stringent specifications for boron (it is less than 1 μg.g^{-1} for fuel material in thermal reactors). Therefore, an accurate knowledge of boron content in nuclear fuel materials and other reactor materials is essential.

While boron presence is detrimental in some cases as mentioned above, it is also used for controlling the excess reactivity for safe operation of the reactor. Boron is one of the elements to possess nuclear properties, which warrant its consideration as neutron absorber material. Boron and its compounds are extensively used in nuclear industry for application as control rod, human shielding against neutrons and as sensor elements. Neutron absorption of boron is sufficiently high in the low neutron energy range to make it an excellent candidate for use in thermal reactors. At higher energies, the cross section of most of other elements become very small, often abruptly as in the case of cadmium, whereas that of ^{10}B, decreases monotonically with energy. Absolute cross sections for neutron absorption along the entire energy spectrum are of sufficient magnitude to make it very effective in the intermediate and also in the high energy range. Boron has another advantage over other potential neutron absorption materials. The reaction products of neutron absorption namely helium and lithium are formed as stable, non radioactive isotopes. As they do not emit nuclear radiation, decay heat problems during reactor shutdown and transfer of depleted control rods are minimal. Considering these attractive properties of boron, boron doped zirconium niobium alloys are used for controlling the excess neutron reactivity in advanced nuclear reactors. For effective utilization of these materials and for absolute neutron reactivity calculation inside nuclear reactor core, boron content has to be determined in these materials. In addition to the total boron content, its distribution over entire length of material rod is also essential for nuclear physics calculations. An accurate knowledge of boron content with its associated uncertainty is absolutely required for the reactivity calculations.

In the back-end of fuel cycle, the radioactive waste generated contains host of radionuclides produced in nuclear fission may have environmental concerns. Cesium and strontium are two important fission products present in this radioactive waste that are responsible for MANREM problems. These are long lived and heat generating radionuclides. It is estimated that the cumulative spent fuel, arising from existing nuclear reactors all over the world, could be around 3.5×10^5 tons by the year 2010. In this, the yearly yield for ^{137}Cs alone is estimated to be around 27 MCi [1]. Due to long half life ($t_{1/2}$ = 31.2 year) and reasonable thermal output (0.42 W/g), ^{137}Cs has a potential application as the source in gamma irradiators, which are used in environment pollution control, food preservation and sterilization of medical accessories. Due to the toxicity of cesium and its ability to displace potassium from muscles and red cells, removal of cesium from medium and low level nuclear wastes is also desirable. Removal of ^{137}Cs from nuclear waste facilitates the safe and less expensive methodologies for disposal of high-level waste in deep geological repositories as vitrified waste. Hence lot of research is going on to develop a suitable reagent or technique to remove effectively the Cs from nuclear waste. To assess the separation efficiency of a technique, Cs has to be determined.

1.5. Current status of analytical methodologies for boron and cesium determination

1.5.1. Determination of boron

The most commonly employed methodologies for the determination of boron in nuclear technology are atomic emission spectroscopy in combination with either direct current arc or inductively coupled plasma as an excitation source. Fundamental aspects and details of these techniques for the determination of boron are given below.

1.5.1.1. Atomic Emission Spectroscopy

Atomic emission spectroscopy (AES) is a workhorse in analytical spectroscopy for simultaneous multi element determination. In this method, the analyte elements in a given sample are atomized and excited to higher excitation states employing an excitation source. Each element emits its own characteristic light when it's coming to the ground state from the excited state. From the intensity of this characteristic emitted light, concentration of the respective element is determined. The spectral excitation sources used in AES are flame, direct current arc (D.C. arc), alternative current spark (A.C. Spark) and plasma sources such as D.C. plasma, inductively coupled plasma (ICP), capacitively coupled plasma (CCP) and microwave coupled plasma (MIP). The present day atomic emission spectrometry predominantly uses ICP as an excitation source because of its good sensitivity for large number of analytes including refractory elements, large linear dynamic range and the best precision of determinations attainable by any of the spectroscopic techniques. However, in ICP source, only liquid samples are analyzable. Hence, for highly refractory solid sample analysis, which cannot be dissolved in easily, DC arc source is preferable.

For the determination of boron and other trace elements in various nuclear fuel materials there is a need for physical or chemical separation of major host material. Otherwise, the rich emission line spectra of the matrix element could mask the analyte lines, making the determination of the analytes at trace concentrations virtually impossible. Use of ICP as an excitation source in case of trace metal analysis in nuclear fuel materials requires development of chemical procedure for the separation of analytes from the major matrix in order to avoid spectral interferences [2]. For analytical purposes, the chemical separation procedure should be such that the major matrix should be removed to residual level of a few micrograms without loss of analytes of interest. The use of chemical separation procedure in analysis can lead to a few problems like possibility of contamination of trace elements during processing of separation, partial loss of element of interest during acid dissolution and also due to partial extraction to organic phase during major matrix separation. The use of DC arc excitation source in AES involves physical separation of major matrix by halide carrier distillation.

In AES, the signal intensity not only depends on transition probability of the emission line of analyte but also on many other factors such as sample introduction efficiency, temperature and electron pressure of plasma and ionization potential of element of interest. Sample introduction efficiency is affected by viscosity of sample being introduced in solution form. In case of solid samples, electrode temperature and volatility of analytes and other constituents of the sample affect transfer efficiency. For an analyte atom to emit its characteristic line spectrum, first it has to be separated from the matrix, dissociated and vaporized. These processes are governed by the temperature of plasma or excitation source. Temperature and electron pressure of excitation source along with ionization potential of the element of interest define relative concentrations of atomic and ionic species. Many of the properties are interdependent and hence AES based methods cannot be used as absolute methods of determination. All these methods are used as comparative methods wherein measured analyte signal is compared with the signal obtained for a series of standards having matching physical and chemical characteristics with those of the sample.

1.5.2. Determination of cesium

1.5.2.1. Gamma spectroscopy

^{137}Cs is a radioactive isotope of cesium which is formed as a fission product in nuclear fission of uranium and plutonium. It has a half-life of about 30.17 years, and decays by beta emission to a metastable nuclear isomer of barium, ^{137m}Ba (about 95 percent of the nuclear decay leads to this isomer. The other 5 percent directly populates the ground state, which is stable.) $^{137\,m}$Ba has a half-life of about 153 seconds, and it is responsible for all of the emissions of gamma rays. Decay mechanism is shown in figure 1.1. One gram of caesium-137 has an activity of 3.215 tera Becquerel (TBq). The photon energy of ^{137m}Ba decay is 662 keV. Due to huge difference in half lifes of ^{137}Cs and ^{137m}Ba, secular equilibrium is developed in decay process of these isotopes. Hence by measuring the intensity of γ ray at 662 keV of energy employing gamma ray detectors based on high purity germanium (HPGe) in association with multi channel analyser, cesium activity and then its content could be calculated. Generally, by measuring the activity of ^{137}Cs, cesium content in radioactive waste streams determined. Also using this isotope as a tracer, separation efficiency of cesium employing various extractants was determined [3,4]. This techniques based on gamma spectrometry offer very sensitive measurement option. However, obtaining radioactive Cs isotopes and its measurement may not be possible to all researchers.

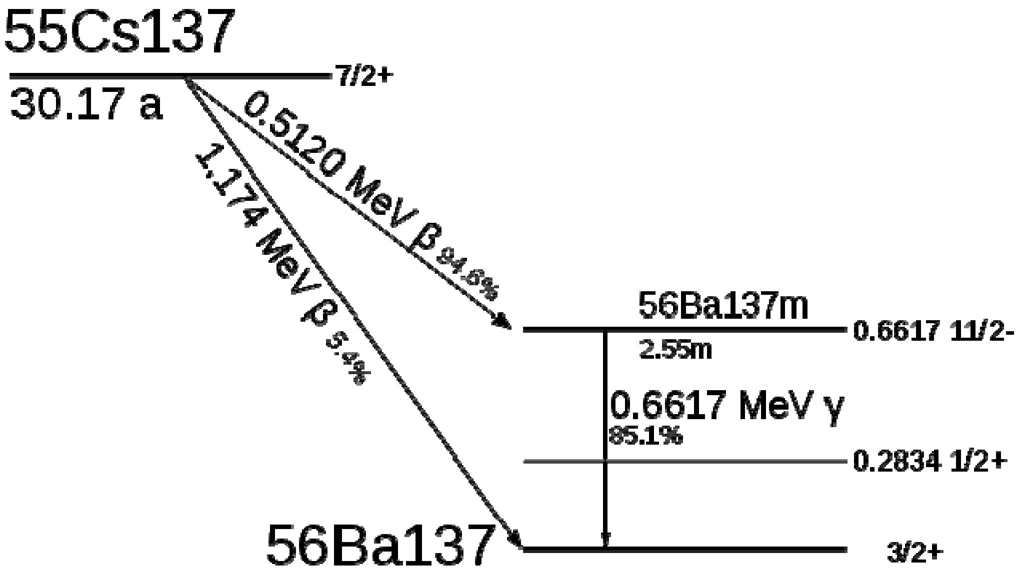


Fig 1.1. Decay mechanism of ^{137}Cs isotope.

1.5.2.2. Atomic absorption spectroscopy

In this methodology, solution containing Cs (preferably in HNO_3 medium) of about 5 μL loaded on carbon rod atomizer of electrothermal atomization- atomic absorption spectroscopy (ETA-AAS). The sample will be heated to 150 °C for drying and then for making ash. Finally it will be heated 2400 °C for atomization. Absorbance of Cs atom was measured at 852.1 nm using photo multiplier tube with deuterium lamp as an emission source [5]. Even though, it is very sensitive methodology for Cs determination, it involves expensive instrumentation and high cost of operation.

1.6. Scope of the present work

A number of analytical methodologies do exist for the determination of trace elements such as boron and cesium. But there is still enough scope either for modification of existing methodologies or development of new ones. Even though, instrumental techniques like DC arc AES, ICP-AES and AAS are sensitive, possess multi-elemental analysis capability and are deemed to be workhorses for this purpose, they require matrix matched reference materials. Many times, matrix matched standards may not be available or are not accessible. Moreover, boron being a critical trace constituent it is desirable to have the measurement carried out with as much high precision and accuracy as possible, identifying all the possible sources of uncertainties to arrive at statistically acceptable expanded uncertainty in its measurement. With the multi-elemental techniques mentioned above, precision achievable is poor. It is desirable to look for alternate methods in which the requirement of matrix-matched reference materials is not that critical. Moreover, boron being a critical trace constituent it is desirable to have the measurement technique with as much high precision and accuracy as possible. Hence, there is a definite scope for developing alternative methodologies for the determination of boron from various nuclear fuel materials and other reactor components. Determination of boron from diverse matrices such as uranium based fuel materials, alloys, refractory materials like Zr-Nb is truly a challenging task as a single analytical method alone would not be applicable. An attempt has been made in the present investigations to develop analytical methodologies for boron determination based on independent analytical principles. Different analytical techniques not only enable the analytical scientist to encompass diverse sample matrices but also obviate the need for reference materials.

Even though radioactivity counting techniques based on gamma spectrometry offer very sensitive measurement option, however, obtaining radioactive Cs isotopes and its measurement may not be possible to all researchers. It would be ideal to have a measurement technique which is reasonably sensitive, easily portable and at the same time can be applicable to measurement of stable cesium also. One approach that offers rapid, reliable measurements in aqueous environments is the polymeric membrane ion selective electrodes (ISEs).

Present investigations are therefore focused on (i) development of various methodologies to determine boron content present in various materials of interest in nuclear technology and (ii) development of ion selective electrode for cesium employing various calixarene compounds.

Theoretical principles and brief description of various analytical techniques used are given below.

1.7. Boron determination

1.7.1. Prompt Gamma Neutron Activation Analysis (PGNAA)

Prompt Gamma Neutron Activation Analysis (PGNAA) is a nuclear analytical technique for the analysis of elements present in solid, liquid and gaseous samples by measuring the capture gamma rays emitted from the samples during neutron irradiation. PGNAA is one of the sensitive methods to determine boron in various matrices [6]. Since it is a matrix independent technique, matrix matched standards are not essential for each and every analysis. Moreover, it's a one of the preferable methods as a reference for certifying the value in any standard.

Capture gamma rays also called prompt gamma rays since they are emitted within about 10^{-12} s of capture of neutron by an atomic nucleus. So neutron irradiation and gamma ray counting of the sample is done simultaneously in PGNAA. It is therefore an online technique and preferably requires a "neutron beam" facility for irradiation of targets. On the average 3-4 γ rays are emitted per neutron capture and they carry off about 7-10 MeV excitation energy, which is the average binding energy of a neutron in a nucleus. The prompt gamma rays can therefore have energies in the range of a few keV to about 10 MeV. Prompt gamma rays are characteristic of the isotopes of elements and practically all isotopes of all elements absorb neutron and emit prompt gamma rays. Hence, all elements in entire periodic table can in principle be measured employing prompt gamma rays. However, it is one of the suitable methods to determine low atomic number elements like H, B, C, N, Si, P, S and Cl and elements like Hg, Cd, Sm and Gd which are having large neutron absorption cross section. The main advantages of this technique are i) non-destructive multi-elemental bulk analysis is possible which offers the flexibility of sample size and shape and can be particularly suitable for archeological, geo and cosmo-chemical analysis, ii) because of higher γ ray energy there is a minimum attenuation in the sample and hence larger sample size can be used for analysis.

The main limitations of this methodology are (i) the prompt gamma ray spectra are very complex, often containing several hundred peaks necessitating the use of a suitable peak fitting software, (ii) a separate neutron beam facility is required, (iii) existing prompt gamma ray data are inadequate and (iv) sensitivities for most of the elements are lower than the conventional neutron activation analysis.

As mentioned above, dedicated neutron beam facility is required for PGNAA. In general neutron beam lines used for prompt gamma experiments can be broadly classified as

1.7.1.1. Guided Beam

Here neutron beam is transported from reactor core to experimental site through a beam tube. This offers the following advantages: (1) low stray neutron and gamma ray background (2) both thermal and cold neutron beam can be used (3) minimal interference from fast neutrons due to resonance. Cold neutron beams offer higher sensitivity due to higher beam intensity and enhanced absorption cross section arising from 1/v law.

1.7.1.2. Diffracted Beam

Neutron beam coming out of reactor core is reflected by a suitable crystal and taken to the experimental site. In this case also high gamma ray background of the radial neutron beam is avoided. Here is beam is composed of neutrons having selective wavelength.

1.7.1.3. Spallation Neutrons

Neutrons emitted from a spallation reaction in a cyclotron are thermalised and used as a beam. The characteristic of such beam is that there is no gamma ray background associated with a reactor and higher neutron beam intensity is also realised.

1.7.1.4. Shielding requirements

Since stray neutron and gamma ray background are usually very high around a neutron beam line, detector shielding is an important aspect of PGNAA set up. Gamma ray background is reduced using a thick lead shield while neutron absorbers like Cd and B can be used for neutron shielding. However, B and Cd produce 478 keV and 559 keV (and higher energy) γ rays respectively on neutron absorption which contribute to the background. Neutrons also react with detector cover cap and Ge to produce ambient gamma ray background. Hence enriched ^{6}Li in the form of LiF ceramic tile or in other form is commonly used as cover cap of the detector to prevent neutron from entering the detector. ^{6}Li (n, α) ^{3}T reaction does not produce any γ ray.

1.7.1.5. Target preparation and irradiation

Normally solid targets in the range of 0.1 to 1.0 g in powder, pellet or disc are used for irradiation. For liquid samples upto 2 mL could be taken and also it depends on the volume of sample holder and neutron beam size. Size of the target should be less than the neutron beam size. If comparison with a standard is done, then errors due to matrix effect (neutron self shielding, neutron scattering, gamma ray attenuation and change in detector efficiency due to sample geometry) can be minimized by matching geometric configurations of sample matrix as closely as possible to that of standard. For irradiation, samples are usually wrapped or sealed into Teflon bags and suspended in the neutron beam using Teflon string. Teflon produces minimum background since both carbon and fluorine have low neutron absorption cross section (in the order of mb).

1.7.1.6. Instrumentation

The instrument used for PGNAA should be a high resolution, high efficiency γ ray spectrometer system. Generally high energy γ rays will be emitted in PGNAA analysis. Hence, a large volume high purity germanium detector is required to meet the requirement of PGNAA analysis. In order to reduce the Compton background in the spectra, the HPGe detector is often used with an anti Compton annular BGO (bismuth germanate) shield which surrounds the HPGe detector. Since a Compton scattered gamma ray from HPGe detector is intercepted by the anti Compton shield, the signal from HPGe detector is rejected if it is associated with a signal from the shield [7, 8]. Thus Compton background could be appreciably reduced, which in turn improves the detection limit of measurement. Since, pair production becomes the primary mode of interaction for high energy γ rays in the detector material, higher energy portion of the prompt gamma spectrum is complicated by the presence of single and double escape peaks in addition to photo peaks. Thus every γ ray produces three peaks. In order to reduce the complexity, the anti Compton shield is also used in pair spectrometer mode. In this case, the coincidence signal from the two segmented halves of the shield in association with HPGe detector signal is registered as valid event. Thus the higher energy portion of the spectra becomes free from the photo peak and single escape peak, thereby making the spectra simpler. In practice, data acquisition is simultaneously carried out in singles, anti Compton and pair mode and sorted out during data analysis time. Data acquisition is done in a pulse height analyser (PHA) with 8k memory.

1.7.1.7. Methodology

The count rate R (cps) due to i^{th} isotope of an element present in the sample is given as

$$R\ (\text{cps}) = W\theta_i N_o \sigma_i \phi a_i \varepsilon_i / M \quad \ldots\ldots. (1)$$

Where W is weight of the element in the sample, and M is its atomic weight. θ_i, σ_i and a_i are the isotopic abundance, cross section and gamma ray abundance of the i^{th} isotope of the element of interest. ε_i is efficiency of detection of gamma ray of interest. N_o and ϕ are Avogadro number and flux of the neutron beam respectively. As evident from the equation above, the detection sensitivity of an element is given by the product $(\theta_i\sigma_i\phi a_i\varepsilon_i)$ and higher value of any one of the parameters enhances the sensitivity of detection.

Four different methods can be used to carry out elemental analysis using PGNAA. They are

i. ***Absolute method*:** In this method, the measured count rate due to an isotope is directly converted to weight (W) of the corresponding element in the sample using the equation

$$W\,(g) = R(cps)\,M\,/\,(N_o\theta_i\sigma_i\phi a_i\varepsilon_i) \quad ......\,(2)$$

The method requires the knowledge of neutron flux, literature value of $\sigma_{i,}a_i$ and experimental determination $\varepsilon_{i.}$ This method is not used in practice due to variation of neutron flux at experimental site with time and non availability of reliable data of $\sigma_{i,}a_i$ in literature.

ii. ***Relative method:*** In this method, weight of an element (W_a) in a given matrix is determined with reference to a standard (W_s) using the relation:

$$Wa = W_s\,(cps)_a/(cps)_s \quad ....(3)$$

Advantage of this method is that flux monitor and nuclear constants are not required. The disadvantage being, sample and standard cannot be irradiated together so the matrix effect (self absorption and scattering) and geometrical difference between sample and standard affect the accuracy. This limitation could be overcome by proper planning of the experiment. This method is commonly employed for analysis.

iii. ***Single comparator (Mono standard) method:*** One can obviate the need of multi-elemental standard by the use of mono-standard method, also known as k_o standardization method. In this approach, the sample is co-irradiated with a suitable comparator element like chlorine (salt form) or titanium. In order to use this method for elemental analysis a k_o factor, which is a measure of elemental sensitivity ratio of the isotope of element of interest(x) to the comparator (c), corrected for the efficiencies, has to be determined in advance. The factor is given as

$$K_{o,c}(x) = (A_{sp}/\varepsilon)_x.\,(A_{sp}/\varepsilon)_c = M_c(\theta_i\sigma a)_x\,/\,M_x(\theta_i\sigma a)_c \,........(4)$$

Here (A_{sp}/ε) refers to specific count rate corrected for the efficiency. The first part is experimentally measured and the second part can be evaluated using nuclear data from standard compilations. The k_o factors or relative sensitivities depend on cross section ratios which depend in turn on neutron spectrum. Thus it is recommended that the factors are determined for a given facility. Once the $k_{o,\,c}(x)$ factors are determined with respect to a comparator, elemental concentration (Cx, µg/g) can be found out using the formula:

$$C_x = \;(A_{p,x}/A_{sp,\,c})\,.\,(1/\,k_{o,\,c}(x)).\,(\varepsilon_c/\varepsilon_x)\ldots\ldots\,(5)$$

Where $A_{p,x}$, $A_{sp,c}$, and ε stand for specific count rate per gram sample, specific count rate per μg of the comparator and efficiency of the detector respectively. Here x and c stand for unknown element and comparator respectively.

iv. ***Internal mono-standard (weight ratio) method:*** In this case, weight ratio of the elements(x) with respect to a comparator element(y) in the sample is determined using the k_o factors

$$W_x/W_y = [A_x/\varepsilon_x k_{o,c}(x)] / [A_c/\varepsilon_c\, k_{o,c}(y)] \ldots\ldots\ldots(6)$$

Here A's refer to observed peak areas. If concentration of the comparator element is determined by some other method or already known then concentration of other elements in the matrix can be obtained for all major, minor elements of the matrix by PGNAA. Absolute concentrations can be found out by material balance equation. This method is truly nondestructive and can be adopted for analysis of samples of irregular size and shape.

Among all these methods, relative method is the most commonly used if matrix matched standards are available for analysis. Since uranium undergoes fission during irradiation with neutron beam and released fission products emit gamma rays in entire region, for the determination of boron in nuclear materials like uranium compounds employing PGNAA, matrix separation is necessary. Selective separation of boron from the matrix will be more effective compared to separation of matrix uranium from the sample.

1.7.2. Separation of boron

Boron from various matrices could be separated employing various processes like distillation [9], pyrohydrolysis [10], ion exchange [11], solvent extraction [12, 13] and chromatography [14]. Amongst these, distillation and solvent extraction are widely employed.

1.7.2.1. Distillation

Distillation procedure is widely used to separate volatile analytes. For separation of boron from various matrices, boron has to be converted to volatile species. For this purpose either methanol or ethanol is used to convert boron to highly volatile methyl or ethyl borate esters. Generally, methanol is preferred due to low boiling point of methylborate ester [15]. For distillation of boron, methanol is added to slightly acidic solution of sample and distilling off the ester and excess of methanol into an absorbing solution. Calcium chloride or sulphuric acid or phosphoric acid is frequently added to the methanol solution to obtain the more nearly anhydrous conditions that favor the formation of the ester. The distillation separation is simple but frequently erratic. Low recoveries are frequently experienced in the presence of many elements, e.g., tungsten, aluminum, chromium, iron and silicon. Multiple distillations are often used, but incomplete recovery under these conditions may still be obtained. Even though it is applied successfully for many analytical purposes, this procedure is tedious, time consuming and plagued by erratic blanks.

1.7.2.2. Solvent Extraction

Boron from various matrices can also be separated, employing solvent extraction with various aliphatic 1,3 and 2,4 diols [16], after converting into boric acid form. Among the various diols, 2-ethyl hexane 1.3 diol (EHD) is widely used for separation of boron due to its high separation efficiency. The structure of ester formed between boric acid and EHD is given in figure 1.2. For efficient separation of boron from matrices generally batch extraction is preferred. Some of the fundamental aspects of solvent extraction and batch extraction are given below.

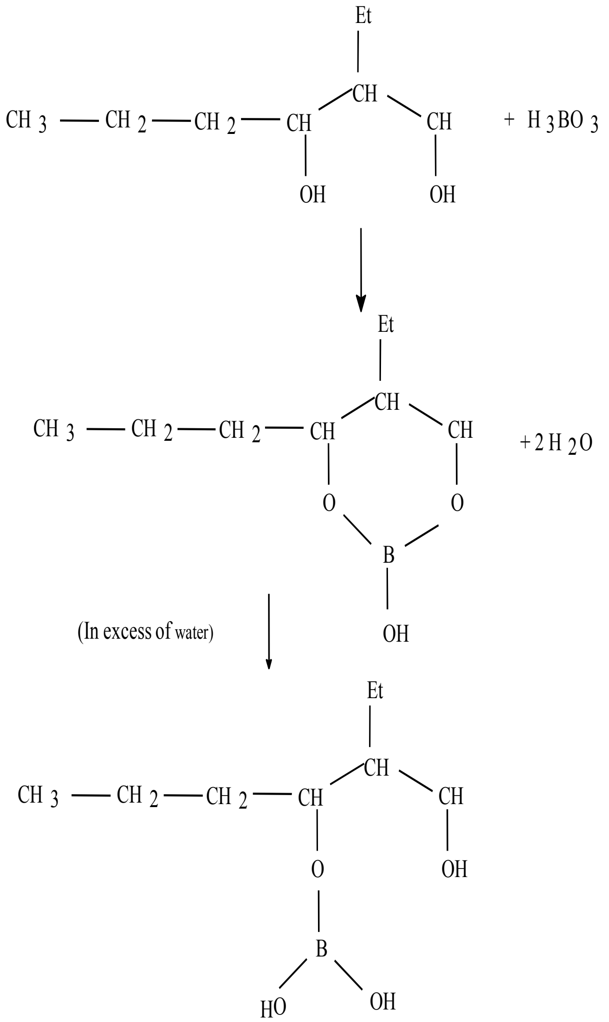


Fig.1.2. Mechanism of solvent extraction of boric acid with EHD.

i. ***Principles of solvent extraction:*** Solvent extraction involves the distribution of a solute between two immiscible liquid phases. A solute S will distribute itself between two phases and within limits, the ratio of the concentration of the solute in the two phases will be constant.

$$K_D = \frac{[S]_1}{[S]_2} \text{........(7)}$$

Where K_D is the distribution coefficient and the subscripts represent solvents 1 (most generally organic) and 2 (aqueous phase). If the K_D value is large, the solute will tend towards quantitative extraction into solvent 1 (organic phase).

In practical experiments different species of solute will distribute between the two liquid phases. Hence instead of considering only one species, we have to consider all the species of the solute which get distributed. It may be mentioned that the ratio of the sum concentrations of all the species of the solute in each phase is constant and it is called distribution ratio (D).

$$D = \frac{[S]_{org}}{[S]_{aq}} \text{......(8)}$$

Here $[S]_{org}$ and $[S]_{aq}$ are the concentration of all the species of the solute present in organic and aqueous phases respectively. The above equation predicts that the extraction efficiency will be independent of the original concentration of the solute. This is one of the attractive features of solvent extraction. It is applicable to tracer levels and also to macro levels alike, a condition that applies only so long as the solubility of the solute in one of the phases is not exceeded and there are no side reactions such as dimerization of extracted solute.

ii. ***The percent extracted:*** The distribution ratio D is constant independent of volume ratio. However, the fraction of the solute extracted will depend on the volume ratio of the two solvents. If a larger volume of organic solvent is used, more solute must dissolve in this layer to keep the concentration ratio constant and to satisfy the distribution ratio. The percent extracted into organic phase is given by

$$E\% = \frac{[S]_o V_o}{[S]_o V_o + [S]_a V_a} \times 100\% \text{....... (9)}$$

Where V_o and V_a are the volumes of the organic and aqueous phases respectively. The relation between %E and D is as given below

$$\%E = \frac{100D}{D + (V_a / V_o)} \text{........ (10)}$$

iii. ***Multiple batch extraction:*** For quantitative analysis, complete separation or quantitative extraction of the solute is required. However, quantitative extraction is not accomplished in a single extraction step even while using an efficient extraction reagent. Maximum extraction is possible by increasing the volume of solvent. However, quantitative extraction is most efficiently carried out in batch extraction mode which involves performing multiple extractions with smaller portions of the same volume of solvent. The amount of solute (W) left in aqueous phase (V_a) after "n" multiple batch extractions with V_o volume of solvent, is given by

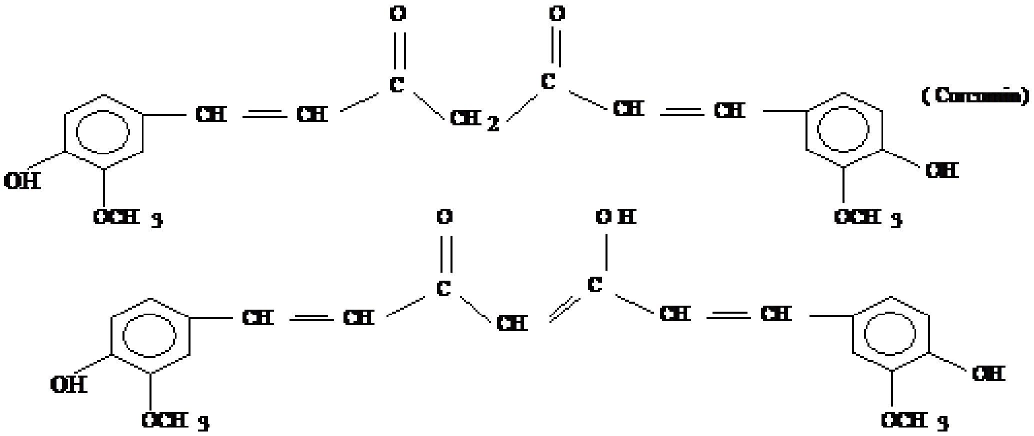
$$W = w_a \left(\frac{V_a}{DV_o + V_a} \right)^n \text{ .... (11)}$$

Here w_a is initial amount of solute present in aqueous phase and D is the distribution ratio.

1.7.3. Spectrophotometric determination of boron

Boron is being a metalloid it cannot be determined directly employing spectrophotometry. Hence a chelating agent which should form coloured complex with boron or boron compounds is desirable and absorbance of boron- chelating agent complex can be measured. In literature a number of reports are available for the determination of boron in various matrices employing spectrophotometry after complex formation of boric acid or tetraflouroborate with Curcumin [17], Carminic acid [18], 1-(2,3,4-Trihydroxybenzylideneamino)-8-hydroxynaphthalene-3.6-disulfonic acid [19], Methylene Blue [20], Crystal Violet [21], 1-(2-hydroxy-3-methoxybenzylideneamino)-8-hydroxynaphthalene-3-6-disulfonic acid (HMOA) [22], Chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulphonic acid [23], Pthalene violet [24], Alizarin Red S, Quinalizarin, Azomethine-H [25] and many more. Among all these compounds, curcumin is preferred due to its high sensitivity and complex stability with boric acid. Complex formation mechanism between curcumin and boric acid is given in figure 1.3.

Even though, complex of boron with curcumin is very stable, in the presence of water it will undergo hydrolysis. Hence we have to maintain non aqueous environment for complex formation and measurements. Also several other ions like Ti, W, Mo and Fe are reported to form complex with curcumin similar to boron [26]. These complexes also have absorbance at same wavelength of boron-curcumin complex (550 nm). Hence separation of



Enal form in acetic acid medium

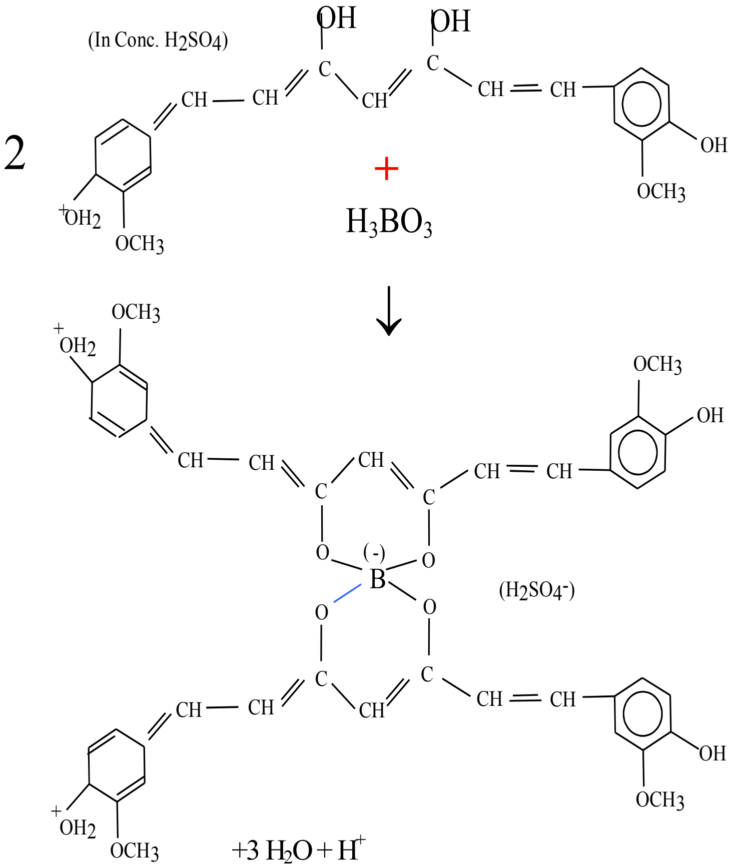


Fig. 1.3. Reaction mechanism of boron curcumin complex formation.

boron is necessary either prior to the complexation with curcumin or after complex formation with curcumin i.e., separation of boron-curcumin complex. To decrease the blank absorbance and to get better precision and accuracy, separation of boron prior to the complex formation with curcumin is preferable. As mentioned above, solvent extraction with 2-ethyl hexane 1,3 diol is preferable over other separation procedures due to simplicity and ease of operation. To avoid interference from traces of moisture if any present in the separated solution, conc. H_2SO_4 is used as media for complex formation of boron with curcumin. The role of conc. H_2SO_4 is in figure 1.3 depicting reaction mechanism boron curcumin complex formation.

1.7.3.1. Theory of spectrophotometry

Spectrophotometry deals with the following regions of the electromagnetic spectra: ultraviolet 185-400 nm; visible 400-760 nm; infrared 760-15000 nm while colorimetry is concerned with the visible region of the spectrum. When electromagnetic radiation, either monochromatic or heterogeneous, falls upon a homogeneous medium, a portion of the incident radiation is reflected, a portion absorbed within the medium and the rest is transmitted. The light intensities are expressed as follows: I_o for incident, I_a for absorbed, I_t for transmitted and I_r for reflected radiation. Then

$$I_o = I_a + I_t + I_r \text{ …….. } (12)$$

Eliminating I_r for given air-quartz interface,

$$I_o = I_a + I_t \text{ …….. } (13)$$

The two laws governing absorption are known as **Beer-Lambert law**.

Lambert's law states that when a monochromatic radiation passes through a transparent medium, the rate of decrease in intensity with the thickness of the medium is proportional to the intensity of the radiation. In other words, the intensity of the emitted light decreases exponentially as the thickness of the absorbing medium increases arithmatically. The law may be expressed by the differential equation

$$-dI/dl = kI \text{ …….. } (14)$$

where I is the intensity of the incident light of wavelength λ, l is the thickness of the medium and k is a proportionality factor for the wavelength and the absorbing medium used. Integrating and putting I = Io when l = 0, we obtain

$$\ln(I_o/I_t) = kl$$

$$\text{or, } I_t = I_o e^{-kl} \text{ ….. } (15)$$

Beer's law states that the intensity of a beam of monochromatic radiation decreases exponentially as the concentration of the absorbing substance increases arithmetically. This may be written as

$$I_t = I_o e^{-k'c} \text{ ………. } (16)$$

Where c is the concentration, combining the two equations and changing from natural to common logarithmic scale, we have

$$\log(I_o/I_t) = \varepsilon cl \quad \ldots\ldots. (17)$$

This is the fundamental equation of spectrophotometry and is known as the **Beer-Lambert law.** Here, if c is expressed in mol L^{-1} and l is in cm, ε is known as the **molar absorption coefficient or molar absorptivity**. It depends on the wavelength of the incident radiation, the temperature and the solvent employed. $\log(I_o/I_t)$ is the **absorbance**, A of the medium. I_t/I_o is the fraction of the radiation transmitted by a thickness l of the medium and is called the **transmittance**, T.

1.7.3.2. Basic Instrumentation

An optical spectrometer is an instrument possessing an optical system, which can produce dispersion of incident electromagnetic radiation, with which measurements can be made of the quantity of transmitted radiation at selected wavelengths of spectral range. A photometer is a device for measuring the intensity of transmitted radiation or a function of this quantity. When combined in the spectrophotometer, the spectrometer and the photometer produce a signal that corresponds to the difference between the transmitted radiation of a reference material and the transmitted radiation of the sample, at selected wavelengths. In the present study, CARY 500 Scan Uv-Vis-NIR spectrophotometer has been employed.

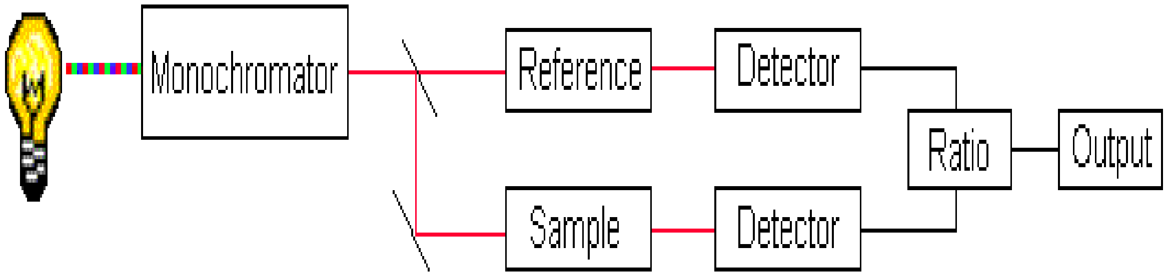


Fig 1.4. Block diagram of spectrophotometer.

1.7.4. BF_4^- ion selective electrode method

Tetrafluoroborate ion selective electrode (BF_4^- ISE) method is one of the sensitive and fast methods for determination of boron. In this methodology, boron present in the sample has to be converted to BF_4^- quantitatively and the response of BF_4^- ISE was measured.

Details about history of ion selective electrode development, working mechanism and practical issues related to ion selective measurement are briefly discussed in cesium ion selective electrode development part of this chapter.

1.8. Determination of Cesium - Ion selective electrode

1.8.1. History of ion selective electrode development

The historic discovery of selective potentiometric transducers was achieved by Cremer about one hundred years ago [27]. 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 [28]. The potentiometric response of membranes that consist of various non-glass materials have been investigated by several groups [29-31]. 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 [32] 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 [33], 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 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 [34] The first neutral ionophore molecule, the antibiotics valinomicin and nonacin, 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.

1.8.2. Principle of Ion selective electrode

The typical schematic diagram of membrane based ion selective electrode (ISE) setup is given in figure 1.5. 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.

$$E = \text{Constant} + \frac{2.303\ \text{RT}}{\text{zF}} LogA \qquad \text{........ (18)}$$

Here 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.

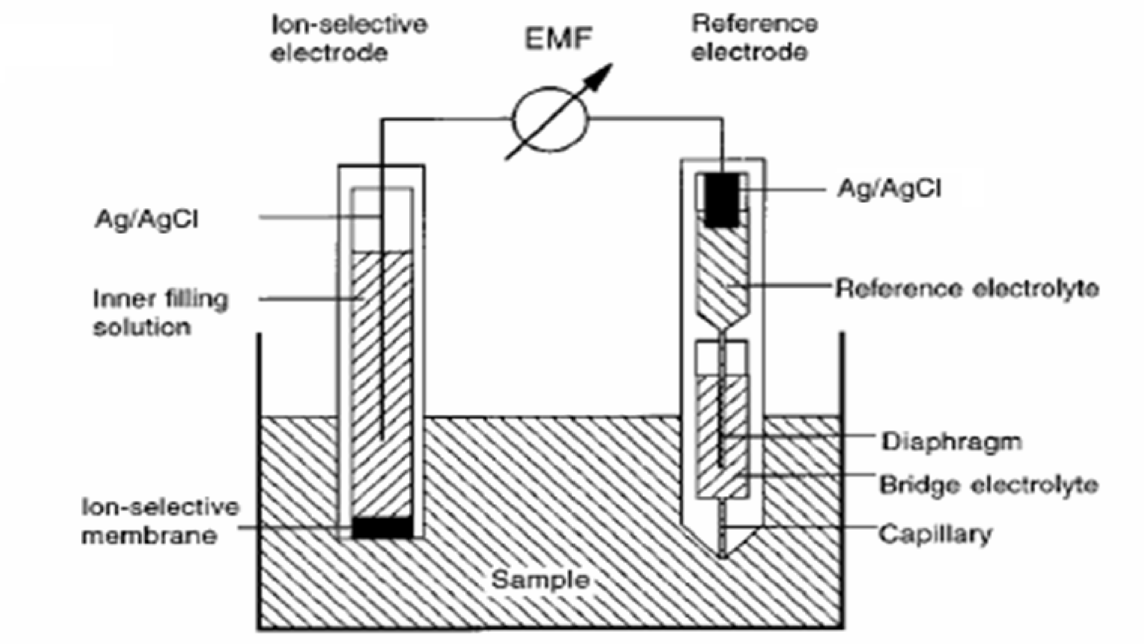


Fig.1.5. Schematic diagram of ion selective electrode measuring circuit and cell assembly.

The ion sensitive polymeric membrane is a water immiscible liquid of high viscosity commonly placed between two aqueous phases. The essential part of the polymeric membrane based ISE is choosing suitable reagent or complexing ligand to form a complex, selectively with element of interest. This reagent is called ionophore. Along with ionophore, other constituents like lipophilic salt as ion exchanger, plasticizer to maintain mobility of ionophore in the membrane and finally the matrix to hold all these substances. The ISE responds to the activity of the target ion and usually covers the range from about 1 to 10^{-6} M. Its selectivity is related to equilibrium constant of the exchange reaction of target and interfering ions between the organic phase (membrane) and aqueous phase. It strongly depends on the ratio of complex formation constants of these ions with the ionophore in the membrane phase.

1.8.3. The response mechanism

The basic theory of the response of solvent polymeric membrane electrodes was developed many decades ago [35-37]. However, the relevance of the various contributions to the membrane potential has been the subject of long-lasting debates [38, 39]. Ion-selective electrode membranes are typically investigated under zero-current conditions in a galvanic cell such as the following (see Figure 1):

Hg | Hg_2Cl_2 | KCl(sat.) | 3 M KCl || sample solution || liquid membrane || internal filling solution | AgCl | Ag.

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

$$\mathrm{emf} = E_{const} + E_J + E_M \quad \ldots\ldots\ldots (19)$$

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 ion-selective electrodes; the role of the reference electrode on the overall emf measurement should, therefore, not be overlooked [40]

1.8.4. 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 [38, 41]. 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

$$E_M = \mathrm{Const} + E_{PB} \quad \ldots\ldots (20)$$

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:

$$\mu^*_{(aq)} = \mu_{(aq)} + zF\Phi_{(aq)} = \mu^0_{(aq)} + RT \ln a_{I(aq)} + zF\Phi_{(aq)} \quad \ldots\ldots\ldots (21)$$

and for the contacting organic phase:

$$\mu^*_{(org)} = \mu_{(org)} + zF\Phi_{(org)} = \mu^0_{(org)} + RT \ln a_{I(org)} + zF\Phi_{(org)} \quad \ldots\ldots (22)$$

where μ is the chemical potential (μ^o under standard conditions), z is the valency and a_I 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:

$$E_{PB} = \Delta\phi = -\frac{\mu^{o}(org) - \mu^{o}(aq)}{zF} + \frac{RT}{zF}\ln\frac{a_1(aq)}{a_1(org)} \quad \text{........ (23)}$$

Often, the term comprising of the standard chemical potentials is combined to the symbol k_I; i.e., ($k_I = \exp(\{\mu^0\ (aq) - \mu^0\ (org)\}/RT)$. 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 (E_0) and eq 23 reduces to the well-known **Nernst** equation:

$$E = \text{Constant} + \frac{2.303\ \text{RT}}{\text{zF}} LogA \quad \text{....... (24)}$$

According to eq 23 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 [42]. Only within the extremely thin charge separation layer at the very interface, where electroneutrality does not hold, are sample-dependent changes in the concentrations of complex and ionophore and ionic sites allowed to occur.

1.8.5. 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 semiempirical **Nicolskii-Eisenman** equation (N-E equation).

$$E = Cost + \frac{RT}{z_A F}\ln\{a_A + \sum_{B \neq A}^{B} K_{A,B}^{Pot}(a_B)^{z_A/z_B}\} \quad \text{...... (25)}$$

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. $K_{A,B}^{pot}$ is the selective coefficient of ISE for primary ion over interfering ion. For extremely selective electrodes, the **Nicolskii** coefficient $K_{A,B}^{pot}$ 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.

1.8.6. Determination of Selectivity Coefficients. $K_{A,B}^{pot}$

1.8.6.1. 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) [43].

i. ***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 $K_{A,B}^{pot}$ from the equation:

$$K_{A,B}^{pot} = \frac{a_A}{(a_B)^{z_A/z_B}} \ldots\ldots\ (26)$$

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

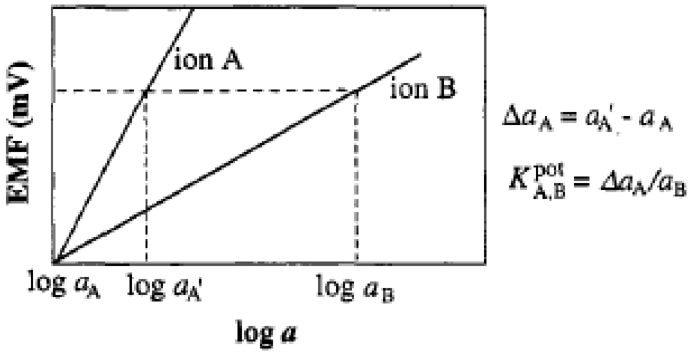
ii. ***Separate solution method*:** The potential of a cell comprising an ion-selective electrode and a reference electrode is measured with each of two separate solutions, one containing the ion A at the activity a_A (but no B), the other containing the ion B at the same activity $a_B = a_A$ (but no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

$$\log K_{A,B}^{Pot} = \frac{(z_A F)(E_2 - E_1)}{2.303RT} + (1-(z_A/z_B)\log a_A \ldots\ldots\ (27)$$

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 [44-49] also with ions of different charge [50]. This suggests that selectivity coefficient is not a physical constant but a value which changes according to experimental conditions.

1.8.6.2. 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 1.6). 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.



$$\Delta a_A = a_A' - a_A$$

$$K_{A,B}^{pot} = \Delta a_A / a_B$$

Fig.1.6. Determination of selectivity coefficients by matched potential method.

1.8.7. 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 loose sensitivity towards the primary ion. According to the IUPAC recommendation of 1976 [38], the detection limit is defined by the intersection of the two extrapolated linear calibration curves (figure 1.7.).

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 [51]. For cation-selective membranes (anion-selective electrodes can be treated in complete analogy), the upper detection limit is a consequence of a co-extraction 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) [52].

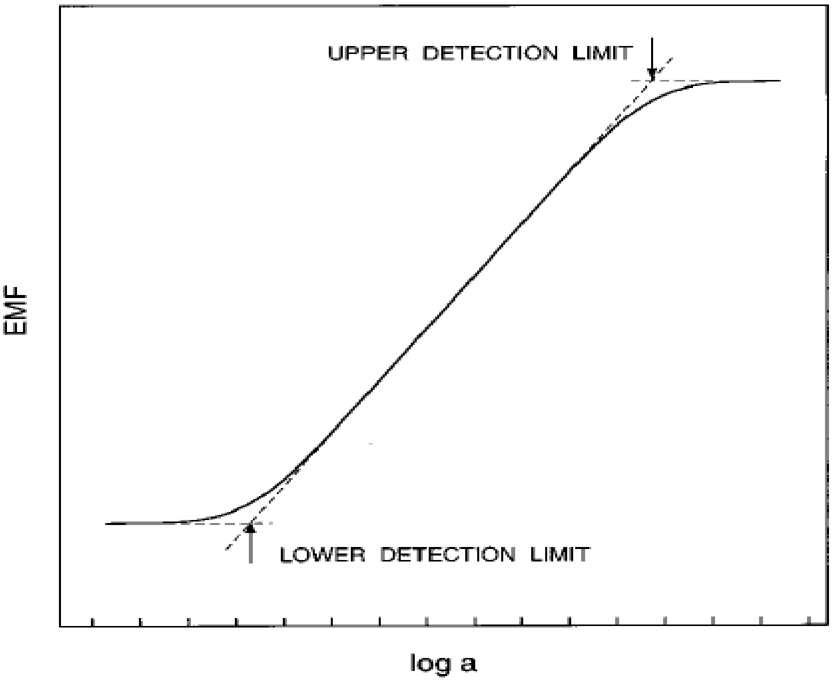


Fig.1.7: Definition of the upper and lower detection limits of an ion-selective electrode according to the IUPAC recommendations.

1.8.8. 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.

1.8.9. 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 ***($\Delta E/\Delta t$)*** 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 [53].

1.8.10. 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.

1.8.10.1. Ionophores

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.

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 10^4 to 10^9 mol^{-1}. kg 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 counterions 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.

1.8.10.2. Ion additives

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.

1.8.10.3. Plasticizer

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 o-NPOE to apolar dibutyl sebacate (DBS) or dioctyl sebacate (DOS) reduces the Ca^{+2} selectivity with the ionophore ETH 1001 by orders of magnitude [54, 55]. 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 [56].

1.8.10.4. 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 [57]. Polymers as homogeneous membrane matrices came first in use with charged carriers [58]. The first neutral-carrier-based polymer ISE membranes were prepared with valinomycin in silicone rubber or PVC [59] 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 [60] 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 [61] as well as by ion exchange and atomic absorption [62], 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 [63], apart from having the necessary solubility, for a polymer to serve as sensor matrix, the most important factor is that its glass transition temperature (T_g) must be below room temperature. With polymers of high T_g (e.g., high molecular weight PVC: T_g 80°C), plasticizers must be used, while with those of low T_g e.g., soft polyurethanes with a low content of crystalline units [64] silicone rubber or poly(vinylidene chloride) [65], polysiloxanes [66] 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.

1.8.11. Issues related to practical application of ISE

1.8.11.1. 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.

i. ***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

$$\Delta E = \Delta E_0 - \frac{2.303\ \mathrm{RT}}{\mathrm{F}} Log a_{Cl^-} \quad .....(28)$$

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^-, S^{2-} 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 KNO_3, $(NH_4)_2SO_4$, CH_3COOLi etc.,).

ii. ***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

$$\Delta E = \Delta E_0 - \frac{4.606\ \mathrm{RT}}{\mathrm{F}} Log a_{Cl^-} \quad \ldots\ldots(29)$$

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.

1.8.11.2. 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

$$a_X = [X]\gamma_X \quad \ldots\ldots\ (30)$$

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 [67] 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 [68]. This equation know as the **Debey-Huckel equation.**

$$-Log\gamma_X = \frac{0.51 Z_X^2 \sqrt{\mu}}{1+3.3 a_X \sqrt{\mu}} \quad \ldots\ldots..(31)$$

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 [69] which can be used to calculate activity coefficient of any ion

$$-Log\gamma_X = -0.511\ z_X^2 \left[\frac{\mu^{1/2}}{(1+1.5\mu^{1/2})} - 0.2\mu\right] \ldots\ldots\ (32)$$

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

1.8.11.3. 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** [70, 71].

$$E^{H}_{j,k} = -\frac{RT}{F}\left[\frac{\sum \frac{C_{i.k}\lambda_i^{\infty}}{z_i} - \sum_i \frac{C_{i.r}\lambda_i^{\infty}}{z_i}}{\sum_i C_{i.k}\lambda_i^{\infty} - \sum_i C_{i.r}\lambda_i^{\infty}}\right] \ln \frac{\sum_i C_{i.k}\lambda_i^{\infty}}{\sum_i C_{i.r}\lambda_i^{\infty}} \quad \text{.........} \; (33)$$

Where C_i is the concentration of ions in equivalents per dm^3, λ_i^{∞} is the limiting equivalent ionic conductance at infinite dilution. The values of the limiting equivalent conductance taken from literature [35] and they are given in table1.1.

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

Cation	Equivalent conductance	Anion	Equivalent conductance
H^+	349.81	OH^-	-198.6
Li^+	38.68	F^-	-55.4
Na^+	50.10	Cl^-	-76.35
K^+	73.50	Br^-	-78.14
Rb^+	77.81	I^-	-76.84
Cs^+	77.26	NO_3^-	-71.46
NH_4^+	73.55	HCO_3^-	-44.50
Mg^{+2}	53.05	CH_3COO^-	-40.90
Ca^{+2}	59.50	SO_4^-	-80.02
Sr^{+2}	59.45	CO_3^{2-}	-69.3
Ba^+	63.63	Formate	-54.59

1.8.12. Calixarenes as an ionophores for Cs^+ ISE

As mentioned earlier, for making any ISE we require an ionophore which will interact selectively with element of interest called primary ion. Characteristics of an ISE like response range, selectivity, life time, response time is mainly depend on a selection of ionophores. Calix[n]arenes have emerged as very attractive building blocks as ionophores in supramolecular chemistry because of their easy large scale preparation, distinctive concave molecular architecture, tunable size of inner cavity and excellent capability of derivatisation. For the last couple of decades, Calixarene compounds have been widely regarded as important class of macro cyclic host molecules, because of their structural and electronic features, which allow a three dimensional control of metal ion complexation, resulting in highly selective and efficient binding properties for specific metal ion [72].

The term "calixarene" was coined by Gutsche [73] in the late 1970s to describe a new class of cyclooligomers formed via phenol-formaldehyde reactions. Each calixarene contains a repeating phenolic unit formed into a macrocycle via methylene bridges. The bridges function as points around which the phenolic groups rotate, leading to various rotamer conformations. Historically, calixarenes are related to resins, such as Bakelite and those investigated by Von Bayer in the 19th century. The calixarene "cups" have a vaselike form defined by an "upper rim, lower rim and central annulus". The nomenclature of these compounds gives the number of repeat phenolic units in enclosed square brackets (e.g., calix[4]arene for a tetramer), with the upper and lower rim substituents being described before and after this stem, respectively.

Analytical chemists are discovering calixarenes because they provide a route to molecules with well defined cavities, which offer simultaneous polar (lower rim) and non polar (upper rim) features. Because of these properties, calixarenes can form inclusion complexes with a wide range of guest species, depending on the binding groups substituted at each rim and the number of repeat units in the macrocycle.

It is well studied that, calix[4] arenes in 1,3 alternative conformation is very selective for cesium. Several reports [74, 75] are available regarding synthesis of calix[4]arenes in 1,3 alternative conformation with various substistuents in lower as well as in upper rims and their application in separation of Cs^+ from various media. However, not enough studies are carried out for making ion selective electrodes employing calix[4]arene compounds. Also, many of the Cs-selective ISEs available or reported in literature have limited lifetime of maximum of a couple of months only. The aim of present work is to develop cesium ion selective electrode employing various calix[4]arenes as an ionophores. Also, one of the aims of present investigation is to fabricate an ISE for Cs with a reasonably long life.

Chapter II

Determination of boron by Chemical PGNAA

2.1. Introduction

2.1.1. Importance of boron in environment and nuclear technology

Boron is one of the trace elements present in water as dissolved salts. Of numerous compounds of boron present, only oxycompounds, in particular boric acid or its salts are soluble in water [76]. However boric acid being a very weak acid (pK_a value of 9.2), has little tendency to transfer protons in aqueous solution. Hence boron will be present mainly as a boric acid in water. In minute quantities, boron is essential to plant life, but larger amounts are toxic to plants and may cause soil sterilization [77]. Hence boron determination in aqueous samples like industrial wastes and sewage effluents is important. Also to establish the salinity of water, boron concentration is one of the key factors [78, 79]. The analysis of boron in aqueous solutions is also required in nuclear technology where boric acid added as a neutron poison in moderator to control excess neutron flux.

2.1.2. Boron determination- PGNAA

To determine the trace amounts of boron in different matrices, various methodologies are available [80]. Prompt Gamma Neutron Activation Analysis (PGNAA) is one of the sensitive methods to determine boron concentration [81- 83]. Briefly, the PGNAA technique involves measurement of characteristic gamma rays, which follow the absorption of thermal neutrons by an isotope of element of interest. ^{10}B occurring in natural boron with an abundance of 19.2%, has an exceptionally large thermal neutron absorption cross section (3846 b). Most of the ^{7}Li (93%) produced by the ^{10}B (n, α) ^{7}Li reaction is in excited state which decays within 5 X 10^{-14} s by emitting a 478 keV gamma ray. Since the gamma ray is emitted while the recoiling ^{7}Li nucleus is in flight, it is **Doppler**- broadened which is prominent in a rectangular energy distribution [81].

Even though PGNAA is a very sensitive technique, pre-concentration is required if the neutron flux available at sample irradiation position, which determines the sensitivity of the method, is low. If the sample matrix is uranium or any other fissile nuclide, it undergoes fission during irradiation with neutron beam and released fission products emit gamma rays in the entire energy region of interest thus causing severe interference. Hence, for the determination of boron in nuclear materials like uranium compounds employing PGNAA, matrix separation is necessary. Selective separation of trace level of boron from the matrix will be effective compared to separation of matrix uranium from the sample. The available neutron flux at sample irradiation position, in the PGNAA setup employed is very low i.e., 10^6 n/cm^2/Sec. Hence, either large amount sample or pre-concentration of boron in the available sample is required for each analysis. In present studies, boron content was determined in ground water samples which are collected from Khuchch, Gujarat, India. Solvent extraction with EHD was employed to separate and pre-concentrate boron followed by its determination by PGNAA. It also describes the standardization, validation of the method and its advantages.

For selective separation and pre-concentration of boron from aqueous medium, solvent extraction with 1,3/ 2,4 diols is preferable [13, 84, 85], because of its high sensitivity, selectivity and ease of operation. In the present method, boron is separated from water samples with 10% 2-ethyl hexane 1,3-diol (EHD) in chloroform employing batch extraction. After evaporation of $CHCl_3$, boron is determined employing relative method of PGNAA by monitoring **Doppler** broadened peak area at 478 KeV.

2.2. Experimental

2.2.1. Reagents

All the reagents used are either Analytical reagent grade or supra pure grade. High purity water obtained from Milli-Q Academic apparatus is used for all the dilutions/preparations of samples. To eliminate the boron contamination, either quartz or Teflon apparatus are used in all experiments.

2.2.2. PGNAA facility

In the present PGNAA system, a reflected neutron beam of energy 0.018 eV from DHRUVA reactor, Bhabha Atomic Research Centre, Trombay, Mumbai is used. A tangential beam of neutrons from the reactor core is reflected by a graphite crystal and taken to the experimental site. The neutron flux at the sample irradiation position is 10^6 n/cm^2/s. Prompt gamma ray spectra are acquired using a Compton suppressed spectrometer consisting well-shielded HPGE- BGO detector, having 40% relative efficiency and 2 keV resolution at 1333 keV of ^{60}Co.

2.2.3. Sample preparation and analysis

10 mL or 15 mL of the ground water sample is taken on the weight basis (depending on the concentration of boron) and acidified with 2 mL of 3 M HCl solution. 2 mL of 10% 2-ethyl hexane 1,3-diol (EHD) in chloroform is added and stirred for 5 minutes with magnetic

stirrer. The mixture was allowed to settle and organic phase was separated by sucking it using a weight burette. The above procedure was repeated four times and the entire organic phase is collected in a quartz beaker. Chloroform from the separated organic phase was evaporated away by heating over a water bath at 80° C, in a fume hood. A blank sample was prepared in the same way by adding all the reagents except sample solution. The residue was quantitatively transferred by using 100 μL N, N-dimethyl formamide into, 1.0 mm thick, 1.0 cm inner dia and 1.5 cm long Teflon container. This sample holder was suspended in neutron beam by a wooden support using Teflon string. Depending the amount of boron present in the sample, time of irradiation was varied from 4000 s to 8000 s for getting good counting statistics. Prompt gamma spectra were acquired online during the sample irradiation. Figure 2.1 depicts gamma ray spectra.

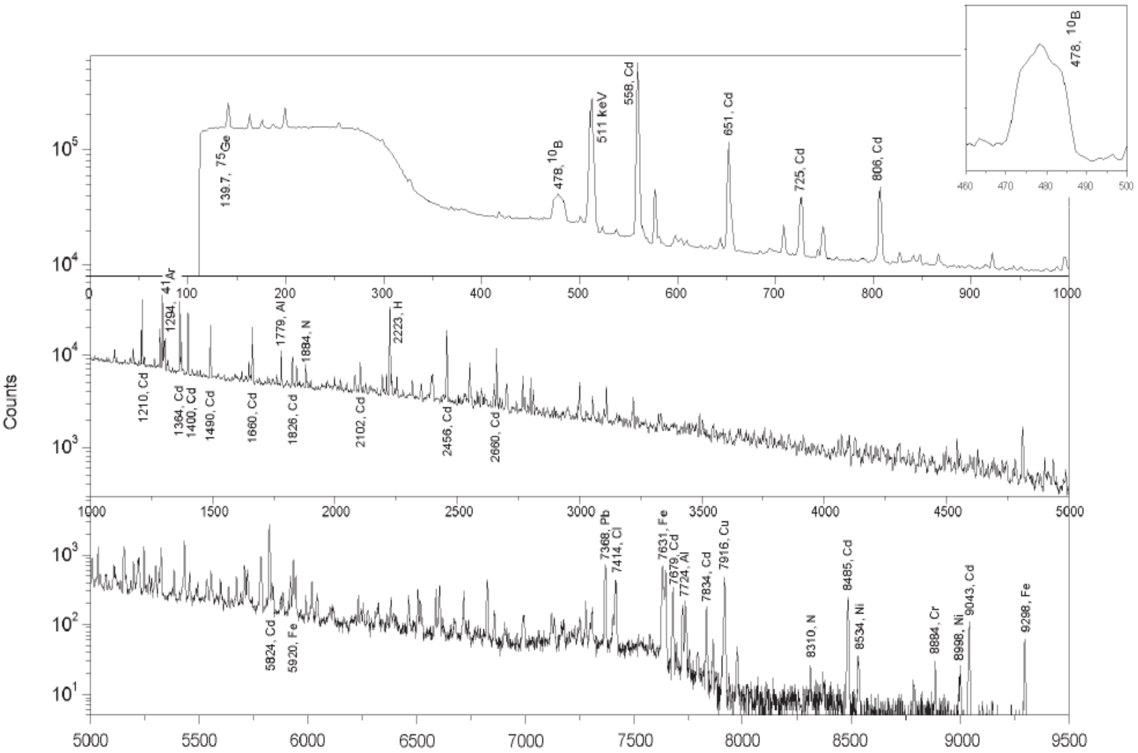


Fig. 2.1. Prompt gamma-ray spectrum of 123.9 μg of boron after chemical separation, counted for 65, 000 s (inset showing the region containing 478 keV peak of ^{10}B)

2.2.4. Calibration plot

A calibration plot between amount of boron and counts/ s is constructed by analyzing different amounts boron from the stock of synthetic boric acid solution employing above procedure. Calibration plot is shown in figure 2.2.

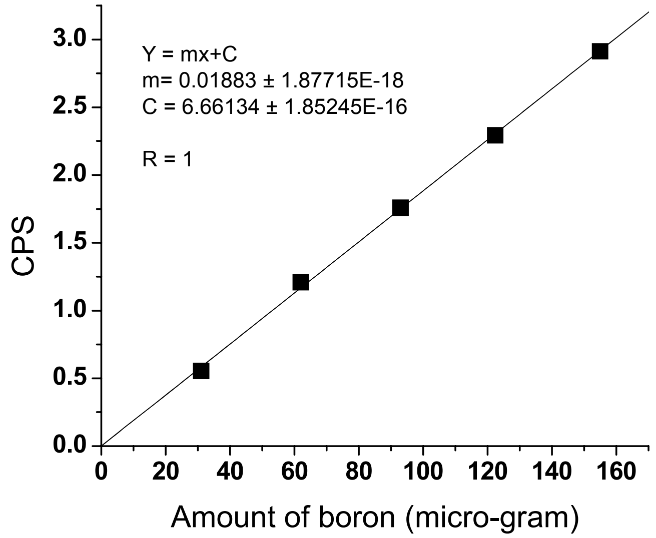


Fig. 2.2. Calibration plot between amount of boron (μg) and background corrected cps.

2.3. Results and Discussion

2.3.1. Quantitative Extraction of boron

For preliminary studies, aliquot of standard boric acid was taken in a quartz beaker containing about 100 μg of boron. 2 M HCl solution was added and then made total volume of the solution was made up to 15 mL with de-ionized water. 2 mL of 10% EHD in $CHCl_3$ was added and stirred for 5 minutes and then separated organic phase was collected in a separate beaker. Again 2 mL of 10% EHD in $CHCl_3$ was added to the beaker containing standard boric acid solution stirred for 5 minutes and then separated organic phase was collected in a different beaker. The above procedure was repeated 5 times and each time the separated organic phase was collected in a different beaker. $CHCl_3$ was evaporated and then measurement was carried out for 4000 seconds after transferring the organic phase to the sample holder as mentioned in the experimental section. It was observed that counts per second (cps) is maximum for first extraction and it was decreasing for each successive separation. After third extraction, there was no further significant decrease in cps and was matching with blank cps. Hence, it could be concluded that, quantitative extraction was observed in three batch extractions. However, four batch extractions were carried out throughout the experiment.

2.3.2. Loss of boron

To study the loss of boron, same amount of a particular sample was aliquoted in two different beakers. After separation of boron with 10% EHD in $CHCl_3$ employing batch extraction, $CHCl_3$ was evaporated from one of the two separated solution at ambient conditions (25 ºC, 1 atm) for 48 hours and from another separated solution, $CHCl_3$ was evaporated by heating in water bath. The rest of procedure was same as mentioned in the experimental section and it was observed that there was no significant difference in counts between these two solutions leading to the conclusion that there was no loss of boron during evaporation of chloroform from the collected organic phase. This is due to the boiling point of B-EHD complex (244 °C) [86] is much higher than that of chloroform (78 °C).

2.3.3. Interference from other elements

In order to obtain precise values of boron concentration, spectral interference at peak area 478 keV due to the presence of other elements was checked. The interference peaks could result from Na (472.2 keV), Si (477.1 keV), Sr (484.8 keV), Cd (477.6 keV), Sm (485.9 keV), Mo (480.9 keV) and Co (484.3 keV). Paul[87] estimated the contribution of some of these elements to the boron peak area using a correction factor with respect to that of reference peak area, which is obtained by irradiating pure interfering elements. The contribution of these elements to the boron peak could be calculated by considering the reference peak area and ratio of k_0 (with respect to the prompt gamma-ray peak of hydrogen at 2223 keV) values of these elements at interference and reference peaks.[88] This practice could be associated with some uncertainty. In the present method, after blank correction at reference peaks of these elements, no significant counts were observed. This shows that absence of these interfering elements in the separated organic phase. This is due to the fact that during the separation, only boron forms complex with EHD and is extracted into organic phase [13]. Hence correction for contribution of these elements to the peak area at 478 keV is not required.

2.3.4. Sensitivity, detection limit, precision and accuracy

From the slope of the calibration plot, sensitivity of the method was calculated and it was found to be 18.83 cps/mg of boron. From the linearity of the calibration plot, it can be concluded that self-attenuation of sample is negligible in calibration range 30- 150 μg. The detection limit of the method [89] was calculated at 3σ level of background area under the peak area of 478 keV. It was 0.7 μg/g for 4000 s counting, 0.5 μg/g for 8000 s counting and 0.2 μg/g for 35,000 s counting for a 15 gram sample size. Since the maximum amount of the sample that can be accommodated in the sample holder of the present PGNAA setup is 1.0 g, the detection limit of the method is 3 μg/g of boron when data were acquired for 35,000 s, without chemical separation. Precision (relative standard deviation at 1σ level) and accuracy of the method was ±5%.

2.3.5. Authentication and validation of the method

The method was standardized and validated by analyzing different synthetic boric acid standard solutions. The results are given in table 2.1. The analytical results of the present method agreed well with the well-established spectrophotometric determination of boron as boron-curcumin complex at 95% confidence interval (*t*-test).

Table 2.1. Determination of boron in synthetic boric acid standards by PGNAA and spectrophotometry

Sample ID	B Concentration (μg/g)	Measured concentration of boron (μg/g)*	
		PGNAA	Spectrophotometry
Standard-01	6.01	6.14 ± 0.31	6.11 ± 0.25
Standard-02	4.46	4.56 ± 0.28	4.57 ± 0.25
Standard-01	5.56	5.45 ± 0.30	5.50 ± 0.29

*Mean of three determinations with standard deviation

2.3.6. Variation of neutron flux at sample holder

To ascertain the consistency of neutron flux, titanium in the form of $FeTiO_3$ was irradiated periodically over a period of 24 hours and the variation in count rate of ^{48}Ti at 1382 keV was found to be 1%. Also synthetic boric acid samples were analyzed at different time intervals during the experiment and reproducibility (within 3%) was observed in boron concentration. Hence, variation in neutron flux during the experiment can be neglected.

2.3.7. Analysis of samples

Employing the present method, concentration of boron was determined in groundwater samples collected from Khuchch, Gujarat, India. The results are given in table 2.2. These results agreed well with those obtained using spectrophotometric method. These results were also validated by another independent method, namely inductively coupled plasma atomic emission spectroscopy (ICP-AES) employing a synthetic boric acid solution as a reference sample for normalization of the results. Seawater sample collected from the

Arabian Sea was also analyzed for boron content and the results agreed well with the reported values [79].

Table 2.2. Determination of boron in water samples by PGNAA, Spectrophotometry and ICP-AES

Sample ID	Determination of boron by PGNAA			Concentration of boron ((µg/g)	
	Amount of sample (g)	Counting Time (S)	Conc. of Boron (µg/g)*	Spectrophotometry$	ICP-AES
Seawater	10.0101 10.0125 10.0095	4000	4.30 ± 0.25&	4.35 ± 0.25	4.10 ± 0.20
Sample-01	9.9997	4000	7.20 ± 0.16	7.50 ± 0.35	7.80 ± 0.40
Sample-02	15.9452	8000	1.68 ± 0.06	1.64 ± 0.08	--
Sample-03	14.9656	8000	1.41 ± 0.05	1.43 ± 0.08	--
Sample-04	15.0505	8000	1.60 ± 0.09	1.55 ± 0.08	--
Sample-05	10.5164	4000	4.18 ± 0.11	4.20 ± 0.20	3.90 ± 0.20
Sample-06	9.9984	8000	2.35 ± 0.10	2.40 ± 0.12	--

*Standard deviation based on counting statistics

$Mean of 4 determinations with standard deviation

&Mean of 3 replicates with standard deviation

2.4. Conclusion

By employing the present method, the concentration of boron was determined in several ground water samples and the results are agreed well with the spectrophotometric determination of boron with curcumin. The possible uncertainty due to correction for the contribution of several impurity elements to boron prompt gamma-ray photo peak, was eliminated by separation of boron by solvent extraction. Employing the present method, boron in nuclear grade uranium compounds (specification limit is less than 1 µg/g) can be determined, where matrix separation is necessary for PGNAA determination of boron. However, 10 g of sample is required due to low neutron flux availability [if the high neutron flux (10^8 n.cm^{-2}.s^{-1}) is available, less than 1 g of sample is sufficient]. The present method may be useful to determine low levels of boron employing radioisotope neutron sources (^{252}Cf and ^{241}Am–Be) where neutron flux is about 10^7 n.cm^{-2}.s^{-1}.

Chapter III

Determination of Boron by Spectrophotometry

Part I: Determination of boron in Ammonium diuranate and uranium peroxide

3.1.1. Introduction

As mentioned in chapter 1 all nuclear materials including U_3O_8 and U metal, are having very stringent specification for boron. Therefore, an accurate knowledge of boron content in nuclear fuel materials like uranium compounds is essential. To monitor the contamination of boron during processing of uranium from its ore, boron has to be determined in intermediate compounds like ammonium diuranate and uranium peroxide, in addition to the final products of uranium. Even though, as discussed in previous chapter, PGNAA is sensitive and also is a reference method for the determination of boron, its sensitivity depends on neutron flux availability at sample holder. In the present setup, the available neutron flux is only 10^6 n/cm^2/sec. Due to this, absolute detection limit of the present PGNAA method is 3µg of boron. Hence for the determination of boron in nuclear materials like uranium metal, uranium oxide and ammonium diuranate which are having specification for boron as <0.3µg/g , huge amount of sample about 10 g is required. Getting this amount of sample for boron analysis is not at all feasible. Hence, there is a need to develop other alternative methodologies to determine boron in uranium compounds. Sah and Brown, in their review article reported several methodologies to determine trace amounts of boron from different matrices [80]. A method based on spectrophotometric determination of trace quantities of boron by curcumin [17, 90- 92] is widely used for routine analysis due to its simplicity and non requirement of matrix matched standards for each analysis. David et al. [93] dealt in detail the chemistry of complex formation between boron and curcumin. To overcome the interference from several ions [94], boron is separated from the matrix either by solvent extraction with 1, 3 / 2, 4 diols [84-85] or by isothermal distillation of borate-alkyl esters [95]. Solvent extraction is preferable for routine analysis due to its simplicity and ease of operation.

Betty and Day [96] determined boron from uranium matrix after extracting it employing 10% of 2-ethyl hexane 1,3- diol (EHD) in $CHCl_3$, followed by color development with curcumin and extraction of boron-curcumin colored complex into methyl iso butyl ketone (MIBK) followed by absorbance measurement. However large amount of sample (2.5 to 3.0 g) was required for analysis and because of high absorbance blank values (0.5 to 0.6), the range of applicability is limited for determination of boron with good precision. For extraction of boron from uranium or any matrix, it is desirable that the sample has to be dissolved. For ease of dissolution of different matrices different acid media are employed. Although spectrophotometric determination of boron with curcumin after solvent extraction with EHD was employed for the last three decades, no data is available for the effect of different acid media on the analytical results. For example, if one wants to recover the precious uranium matrix after the experiment, the acid used for dissolution and subsequent processing has to be considered very carefully. At the same time, it should not lead to any other interferences or complications in the solvent extraction process during separation of boron and its determination with curcumin.

For the chemical quality control of materials of relevance, analytical determinations play an important role. Apart from giving the average value along with the standard deviation of replicate analyses, knowledge of uncertainty in the methodology employed is also essential. Measurement uncertainty is a concept associated with any measurement result and can be used in professional decision processes as well as in judging attributes in many domains, both theoretical and experimental. As the tolerances applied in industrial production become more demanding, the role of measurement uncertainty becomes more relevant while assessing conformity to these tolerances. This is particularly true in determination of critical trace constituent such as boron in nuclear materials, which has stringent specification of only a few $\mu g\ g^{-1}$ or less [97-98]. It may be mentioned that allowed maximum concentration of other metallic impurities in nuclear materials also depends on boron content since total boron equivalent content should be less than 4 $\mu g\ g^{-1}$ for thermal reactors and 7 $\mu g\ g^{-1}$ for fast reactors. Quantitative measurement of boron concentration with all its associated uncertainties is therefore a necessary requirement for appropriate reactivity calculations. Analytical chemists are therefore required to give the quantitative results with a reasonable estimate of uncertainty in the measurement result.

In view of its importance, the International Organization for Standardization (ISO) has given guidelines to compute expanded uncertainty with some examples [99,100]. It is desirable that all the analytical laboratories involved in analytical determinations follow these guidelines to arrive at a correct estimate of expanded uncertainty. Two main approaches to evaluate the measurement uncertainty are the “bottom – up” and the “top - down” assessment procedures [101, 102]. The Top – down approach uses data from routinely undertaken internal quality control measurements, e.g., results of the replicate analyses of certified reference materials (CRM), without identifying all potential sources of uncertainty associated with the method and quantifying uncertainty components. Thus matrix-matched certified reference material with known concentration and uncertainty value is required. Also it does not identify the potential sources of uncertainty associated with the method and does not quantify uncertainty components. Since no matrix matched certified reference material for boron is available with us, the "bottom-up" procedure, which uses each component of the quantification formula of measurand, was employed to evaluate the uncertainty in the measurement result. These include sample preparation such as solid aliquoting from the sample, chemical treatment, absorbance measurement of test portion, evaluation of the measurement, quantification of the analyte along with associated uncertainty In the bottom-up approach the sources of uncertainty in each step of the measurement procedure are identified and the magnitude of each uncertainty component is estimated. It should be mentioned that the use of absolute uncertainties and sensitivity coefficients in the evaluation of uncertainties is preferable, as it permits the combined standard uncertainty to be calculated directly in equations using a wider variety of operations. However, relative uncertainties in the evaluation of combined uncertainty employing uncertainty propagation law may also be resorted to under certain circumstances.

Therefore, the sources of uncertainty in each step of measurement are identified and the size of each uncertainty is estimated. The next stage involves conversion of each uncertainty component (u_i) to relative standard uncertainty and calculation of the combined uncertainty (u_c) using uncertainty propagation formulae. Finally, the expanded uncertainty has been calculated using coverage factor of 2 at 95% confidence level.

In the present method boron was separated from uranium matrix by solvent extraction with EHD in $CHCl_3$ and $CHCl_3$ was evaporated from entire organic phase leaving EHD extract. Colour was developed in this extract by adding curcumin and absorbance measured as reported by Donaldson [6]. Also detailed studies were carried out to (i) investigate the effect of different acid media in the determination of boron and its elimination if any, (ii) study the effect of different diluents on the sensitivity of the method, (iii) establish detection limits for boron determination in uranium and (iv) ascertain the interferences if any, due to other cations and anions. Also combined and then expanded uncertainty in the measurement were estimated employing ISO guidelines.

3.1.2. Experimental

3.1.2.1. Reagents

All the reagents used were of A.R. grade. High purity water obtained from Milli-Q Academic apparatus was used for all the dilutions/preparations of samples. Quartz or polypropylene ware was used to avoid contamination from glassware.

3.1.2.2. Instrument

Cary 500 Scan, Varian, Australia, UV-Vis-NIR double beam spectrophotometer having spectral slit width 0f 0.01 nm at 550 nm wavelength, was used for absorbance measurements.

3.1.2.3. Procedure

Ammonium diuranate is non-stoichiometric and hygroscopic compound. Hence, for precise and accurate determination of boron concentration with respect to uranium, invariably uranium content has to be determined. However, if it is converted to stoichiometric and stable compound, U_3O_8, concentration of boron in uranium can be directly computed. Ammonium diuranate sample was therefore converted into U_3O_8 by heating at 850 ^{0}C in air for 2 hours in an oven. Similarly, uranium peroxide was also converted into U_3O_8 because of its non stoichiometric nature. Aliquots of about 200 mg of U_3O_8 were taken in quartz beakers, treated with 30% H_2O_2, (to convert boron into boric acid) dissolved in 3-4 ml of 3M HCl by heating under I.R. lamp and cooled to room temperature. For uranium metal and uranium dioxide, directly sample aliquots were taken in quartz beakers and they are dissolved with 3M HCl and 30% H_2O_2 by heating under I.R. lamp**.**

Batch extraction was employed for the separation of boron. 1.0 ml of 10% EHD in $CHCl_3$ was added to the sample solution and stirred for 5 minutes with magnetic stirrer. The two phases were allowed to settle and the organic phase was separated. The extraction was carried out four times. From the entire organic phase thus collected, $CHCl_3$ was evaporated by heating to ~70^{0}C in a fume hood. 1.0 ml of 0.375% curcumin in CH_3COOH and 0.5 ml of concentrated H_2SO_4 were then added to this residue. After about 40 minutes, it was diluted with ethyl alcohol or N, N-dimethyl formamide into 25 ml standard polypropylene volumetric flask, for deprotonation of protonated curcumin. The blank experiment was also prepared in the same way by adding all the reagents except the sample. The absorbance of the coloured complex with respect to blank solution was measured at 550 nm by using quartz cell having 1 cm path length. The main contribution of blank value (~0.3) was found to be due to A.R. grade H_2SO_4. This could be minimised (~ 0.2) by using suprapure E-merk H_2SO_4. Calibration plot was obtained by analysing standard boric acid aliquots. If the availability of the sample was limited and the expected boron content was less, lower dilutions to 10 ml (instead of 25 ml) were resorted to realise the desired sensitivity in the measurements. Calibration plots for boron at 100 - 800 ng level (diluted to 25 ml with EtOH) and at for 30 - 350 ng level (diluted to 10 ml with DMF) are shown in figure 3.1.

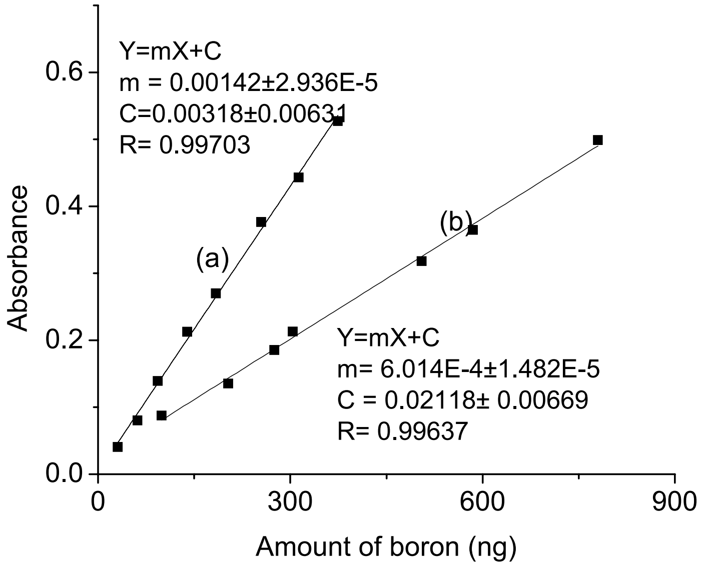


Fig.3.1. Calibration plot for boron determination (R is linear regression coefficient). (a)30-350 ng of boron dilution with DMF for 10 mL (b)100-800 ng of boron for dilution with EtOH for 25 mL.

3.1.3. Results and Discussion

3.1.3.1. Quantitative complex formation between boron and curcumin

Ten aliquots of 0.5 mL of standard boric acid (1.008 μg/g), 4 mL of 3M HCl and 0.5 mL of H_2O_2 were taken in a quartz beakers and heated under I.R. lamp to decompose excess H_2O_2. 3 mL of 10% EHD in $CHCl_3$ was added to all beakers. Stirred for 5 minutes and then separated organic phase was collected in a ten different quartz beakers. After evaporation of $CHCl_3$ at room temperature for about 16 hours, 1 ml of curcumin in CH_3COOH and then 0.5 mL of conc. H_2SO_4 was added to all beakers. After shaking well for 10 minutes, solution from one of the beaker was transferred to 25 ml standard polypropylene volumetric flask quantitatively and then diluted with EtOH. After five minutes above procedure was repeated for second beaker solution. This is continued for every five minutes and upto 55 minutes. Absorbance of all these solutions was measured with respect to water at 550 nm. It was observed that absorbance of the solution was increasing with time of dilution after the addition of curcumin. However, absorbance of solutions diluted after 40 minutes is constant. Hence, it could be concluded that 40 minutes time was required for quantitative complex formation between curcumin and boron in EHD.

3.1.3.2. Quantitative extraction of boron

After conversion of ammonium diuranate to U_3O_8, 200 mg of the sample was aliquoted in a quartz beaker and it was dissolved as mentioned in experimental section. 1 mL of 10% EHD in $CHCl_3$ was added, stirred for 5 minutes with magnetic stirrer and separated organic was collected in a beaker. Again 10% EHD in $CHCl_3$ was added and repeated above procedure and collected separated organic phase in a different beaker. This procedure was repeated six times. Similar experiments were carried out by taking only dissolution mixture i.e. 0.5 mL of 30% H_2O_2 and 3 mL of 3M HCl as blank solutions. After the evaporation of chloroform from all separated organic solution (12 nos) at ambient conditions (25 ºC) for 16 hours, colour was developed with curcumin in the presence of conc. H_2SO_4 and diluted with 25 mL of ethyl alcohol as described in experimental part. Absorbance of each batch extraction solution was measured at 550 nm with respect to same batch extraction of blank solution. Absorbance was maximum for first extraction and it was decreasing with each successive extraction. From fourth extraction onwards there is no significant absorbance (less than 0.0001). Therefore it may be concluded that three batch extractions with 10% EHD in $CHCl_3$ were adequate for quantitative recovery of boron. However, in all the experiments, extraction was carried out four times.

3.1.3.3. Comparison of Diluents

Comparision studies were carried out for the diluents, ethyl alcohol (EtOH) and N, N-dimethyl formamide (DMF), employed in final dilution. There was no significant difference in blank absorbance values measured with respect to millipore water (0.28 and 0.26 with EtOH and DMF respectively) at 25 ml dilution. However at 10 ml dilution, the blank value with DMF was 0.31, which was about half of the value (0.65) obtained with EtOH. This may be due to better deprotonation of curcumin with DMF, which has higher basicity than EtOH (protonated curcumin and curcumin-boron complex absorbs at same wavelength [93]). Reproducibility of blank value was checked at both 25 and 10 ml dilutions, diluted with both EtOH and DMF for six hours, and found that it decreased with time for 10 ml dilution with EtOH only (protonated curcumin decays at the rate of 0.08 mol/h [93]). These observations clearly show that deprotonation of curcumin was not complete with EtOH at 10 ml dilution. Hence in all further experiments for 10 ml dilution, DMF was used. From the slope of calibration plots, the molar absorptivity (ε) values were calculated and found to be 1.66×10^5 l mol^{-1} cm^{-1} and 1.54×10^5 l mol^{-1} cm^{-1} with EtOH and DMF respectively, which are in good agreement with reported values (1.4×10^5 to 2.0×10^5 l mol^{-1} cm^{-1}[92]).

3.1.3.4. Precision and accuracy

The relative standard deviation (precision) for 10 determinations of boron in standard boric acid aliquots was found to be ±3% at 100 ng level with mean of recovery 96% (accuracy 4%). The linear regression was carried out on both the calibration plots. It was very close to unity (0.998). The reproducibility of the calibration plot was checked after three months and same precision and accuracy was obtained.

3.1.3.5. Detection limit of the method

Detection limit of the method was determined by independent replicate analysis of blank solutions (10 Nos) and by using formula [103],

Detection limit of method = $3 \times \sigma_{(blank)}/$ |slope of calibration plot|

20 ng and 10 ng of boron was found as detection limit of the method at 25 ml dilution with EtOH and at 10 ml dilution with DMF respectively.

3.1.3.6. Validation of the method

The modified method has been validated, by analysing boron concentration in Inter Laboratory Comparision Experiments (ILCE) standards of boron in U_3O_8 matrix, where in sample was dissolved in HNO_3 and the matrix separated by solvent extraction with TBP-TOPO (tributyl phosphate- trioctyl phoshonic acid) followed by ICP-AES measurement. The results are presented in table 3.1. As can be seen, by applying statistical treatment of the data (t test), there is no significant difference (95% confidence interval) between the results obtained in the present work and the recommended values.

3.1.3.7. Effect of Different Acid Media

Known amount of boron was taken in the 3M of each of H_2SO_4, HNO_3, H_3PO_4 and $HClO_4$ acid media and determination was carried out employing the procedure standardized. It can be seen from the table 3.2, that strong interference was observed in HNO_3 medium. The spectrum of boron- curcumin complex after extraction from nitric acid medium (Fig.2) also shows the strong interference. Further work showed that, up to 0.2 M HNO_3, the interference was not significant and above 1.0 M, it was significant. To pinpoint whether the interference is from NO_3^-, H^+ or HNO_3, further work was carried out. Boron was analysed after extraction with EHD from solutions containing 3M $NaNO_3$, 200 ng of boron and varying concentrations of H^+ (0-3.0 M of HCl). There was no interference in 3 M $NaNO_3$

medium, indicating that $NaNO_3$-EHD complex is not possibly forming. Above 1 M H^+ in presence of 3 M $NaNO_3$, the interference is significant. This may be due to the formation of HNO_3, which is getting extracted as HNO_3 - EHD complex, similar to B - EHD [8]. Just like nitrate ion [12] the HNO_3 - EHD complex may also be oxidizing or destroying the curcumin. Though HNO_3 is a strong acid, due to equilibrium conditions, some un-dissociated HNO_3 may be available at higher concentrations for ester formation with EHD which is then extracted. Wikner and Uppstrom [104] and Pakalns [105] reported that boron could be determined from HNO_3 medium directly as curcumin complex without solvent extraction after fuming with concentrated formic acid. However efforts to destroy the extacted HNO_3

Table 3.1. Determination of boron in ILCE Boron standards in U_3O_8 matrix.

Sample name	Amount of sample taken (mg)	Present method# Concentration of Boron (μg g^{-1}) ± SD	Reported value* Concentration of Boron (μg g^{-1}) ± SD
ILCE-3	~ 500	0.20 ± 0.01	0.22 ± 0.08
ILCE-4	~ 200	1.21 ± 0.04	1.1 ± 0.24
ILCE-5	~ 300	0.71 ± 0.05	0.77 ± 0.24

Mean of four determinations

*Boron concentration was determined by ICP-AES in nine different laboratories.

SD = Standard Deviation

Table 3.2. Interference studies in different acid media.

Acid Medium	Amounts of B added (ng)	% recovery of boron*
3M H_2SO_4	300	101(1.5)
3M H_3PO_4	300	98 (2.0)
3M $HClO_4$	300	99(1.5)
3M HNO_3	300	40 to 200#

* Mean of 3 determinations are given with standard deviation in brackets.

Since % of recovery is varying from 40 to 200, the standard deviation is not given

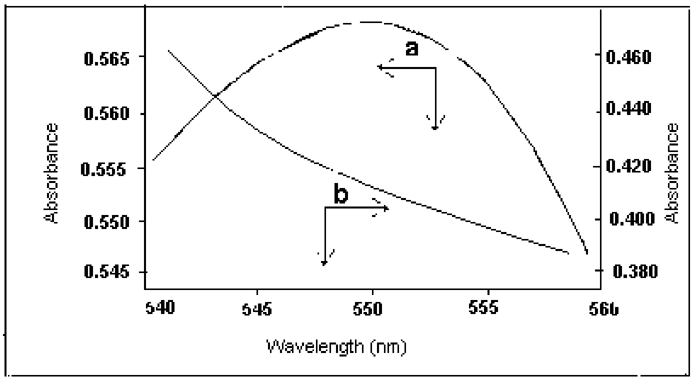


Fig.3.2. Absorbance spectra of boron-curcumin spectra, boron separated from 3M acid media ((a) HCl (b) HNO_3.

by fuming it with formic acid were futile. This may be due to non- reaction of formic acid with EHD-HNO_3 complex. The interference of extracted HNO_3 has been eliminated by its stripping from organic layer with acidified water (0.5 M HCl) which is recycled for each batch extraction. During stripping, HNO_3 - EHD ester may be getting hydrolysed. At lower concentration of HNO_3 (upto 0.2 M), even if it is extracted as HNO_3 - EHD, it will be hydrolysed.

Since the acids, H_2SO_4, H_3PO_4 and $HClO_4$ are not oxidising agents at room temperature, even if extracted into organic phase, they will not interfere in boron determination with curcumin.

3.1.3.8. Interference Studies for Different Elements

Nuclear grade uranium compounds/fuels have stringent specifications for several metallic and non-metallic impurities [97] based on the neutron economy and optimum performance of fuel material in reactor. These impurities may interfere in the determination of boron. Detailed investigations have therefore been carried out to study the interference of several cation and anion species. Ten to fifteen times of the impurity, over the upper specification limit of nuclear grade uranium compounds [97] for 300 mg of sample size was added (which is two to three orders more than that of boron) to standard boric acid aliquots in 3M HCl solution and boron was determined. Results are given in table 3.3. No significant interference was observed at 95% confidence interval (t test). In the flame photometry determination of boron, after solvent extraction with EHD, Agazzi [106] reported interference from Mn, Mo and W even at 20 times of boron content, due to the co-extraction of these elements. Rynasiviz et al. [107] have also reported interference of these elements in direct spectrophotometric determination of boron. Contrary to Agazzi's [106] report, Donalson [92] did not find the interference and inferred that it may be due to the formation of complex of these interfering elements with H_2O_2 or F^-, which were employed in the dissolution of sample. In our studies, F^- was not employed at any stage. In order to study the role of H_2O_2 in the interference of these elements, boron was determined with and without the addition of H_2O_2, in standard boric acid aliquots containing these elements. No significant interference was observed in both cases, indicating that the elements were not getting extracted into EHD. Donaldson [6] reported negative bias if the EHD is more than 0.1ml in the coloured complex formation, however, in our studies no such interference was observed even up to 0.6 ml of EHD.

Table 3.3. Interference studies for different ions.

Element added	Amount of boron taken in an aliquot (ng)	Maximum[#] Specification limit (µg/g of uranium)	Amount added to the aliquot (µg)	% recovery of boron[*]
Al	250	25	80	103(2.0)
Cr	250	25	120	101(3.0)
Mg	250	50	160	100(1.5)
Ca	250	50	160	104(2.5)
Fe	250	100	350	99(1.5)
Mn	250	10	50	96(3.0)
Mo	250	100	350	100(2.0)
F^-	250	10	60	104(3.0)
W	250	100	500	105(2.0)

Depending on the type of reactor (thermal or fast), uranium fuel materials are having different specification limit for the elements.

* Mean of three determinations with standard deviation in bracket.

3.1.3.9. Application of the methodology

After establishing the methodology for the determination of boron from uranium matrix, several ammonium diuranate (ADU) and uranium peroxide samples were analysed. To find out the loss of boron, during conversion of ammonium diuranate and uranium peroxide into U_3O_8, boron was determined in ADU and uranium peroxide before and after conversion into U_3O_8. The concentration of boron (µg /g of U) was calculated (table 3.4) (uranium concentration was determined in ammonium diuranate and uranium peroxide samples by Ti (III) reduction and bi-amperometric titration [108]). No significant difference was observed in both the cases. Therefore it can be concluded that there was no loss of boron during conversion to U_3O_8.

Table 3.4. Boron content in ammonium diuranate (ADU) and uranium peroxide samples (before and after conversion to U_3O_8).

Sample	Concentration of Boron before conversion to U_3O_8* (µg of B/ g of uranium)	Concentration of Boron after conversion to U_3O_8 * (µg of B / g of uranium)
ADU-1	0.75(0.03)	0.74 (0.04)
ADU-2	1.32 (0.06)	1.31 (0.05)
Uranium peroxide-1	0.85 (0.04)	0.83 (0.05)
Uranium peroxide-2	0.92 (0.04)	0.93 (0.05)

* Mean of three determinations with standard deviation in the bracket

3.1.3.10. Estimation of uncertainty

The concentration of boron in sample was determined as

$$B(\mu g.g^{-1}) = \frac{A}{S.w.1000} \quad \cdots\cdots\cdots \quad (1)$$

Where

A = Absorbance

S = Slope of calibration plot (0.00131)

w = weight of the sample in gram. Here 1000 is used to convert ng.g^{-1} to µgg^{-1}

Since standard boric acid aliquots were used to construct the calibration plot, the uncertainty associated with preparation of standard boric acid has to be considered to evaluate the combined uncertainty in the methodology. The combined uncertainty in measurement is categorized into six parts. They are uncertainty in standard preparation (u_{std}), sample preparation (u_{samp}), absorbance measurement (u_{abs}), slope of calibration plot (u_{cal}), repeatability of measurements (u_{rep}) and recovery of measurement (u_{rec}). Since equation 1 involves only multiplication and division of independent quantities, the combined standard uncertainty u_c can be calculated according to the equation

$$u_c = C_m \times \sqrt{u^2_{std} + u^2_{sam} + u^2_{abs} + u^2_{cal} + u^2_{rep} + u^2_{rec}} \qquad \textbf{(2)}$$

where C_m is concentration of measurand, provided each individual uncertainty component is expressed as relative standard deviation. In the present studies, an attempt has made to address the uncertainties arising due to all the components mentioned above. The sources of uncertainty evaluated are given below.

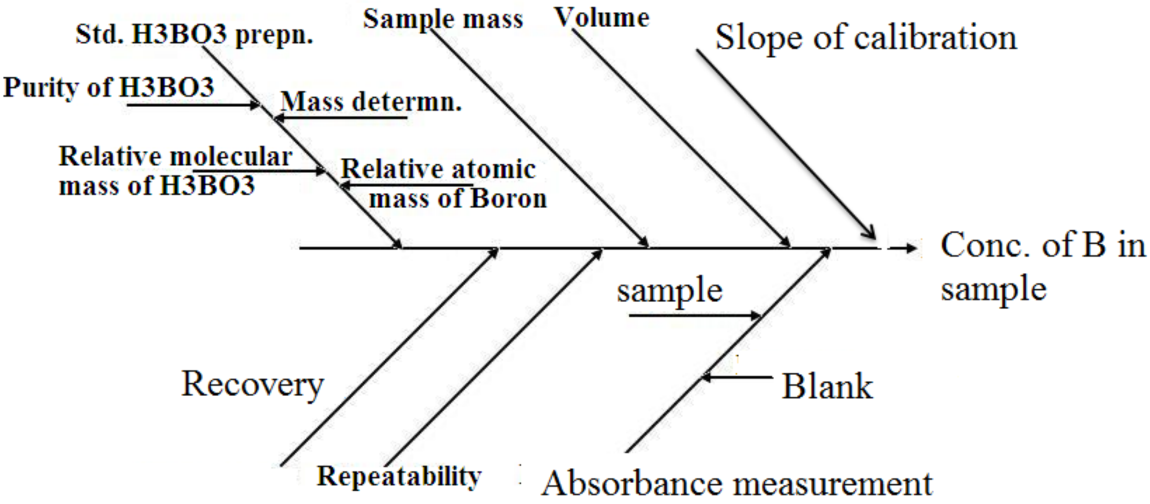


Fig.3.3. Cause effect diagram for determination of boron concentration in U compounds employing spectrophotometry.

i. Uncertainty in standard boric acid preparation:

a. Purity of ortho boric acid: In the suppliers certificate it is given as 99.5 ± 0.5 % pure. The quoted uncertainty is taken as rectangular (uniform) distribution, so the relative standard uncertainty u_1 is equal to $\frac{0.5 \times 100}{\sqrt{3} \times 99.5} = 0.290\%$

b. Mass determination: As quoted by the manufacturer of the balance, the uncertainty in mass determination is 0.2 mg over the entire range. Since 538.8 mg of the ortho boric acid is taken for preparation of standard boric acid solution, the relative uncertainty involved in weighing the standard, u_2 is $\frac{0.2 \times 100}{538.8} = 0.037\%$

c. Molecular weight: The uncertainty in molecular weight of boric acid is arrived at considering the individual element atomic masses and their quoted uncertainties as given by

IUPAC [109]. Rectangular distribution has been applied to quoted uncertainties. The molecular weight of boric acid (61.83302) is calculated using atomic weights of respective elements. The combined uncertainty in the molecular weight of boric acid is calculated employing uncertainty propagation formula and it is 0.004051. The relative combined uncertainty in molecular weight of boric acid, u_3 is $\frac{0.0040516 \times 100}{61.83302} = 0.007\%$

d. Atomic weight of boron: Since standard solutions are prepared as μg of boron per gram of solution, the uncertainty in atomic weight of boron has to be considered. The quoted uncertainty in atomic weight of boron by IUPAC [109] is 0.007 and after applying rectangular distribution it becomes to 0.00404. Therefore the relative uncertainty in atomic weight of boron, $u_{4,}$ is $\frac{0.00404 \times 100}{10.811} = 0.037\%$

e. Dilution: The working standard, employed in all experiments, is prepared by diluting the stock solution appropriately (through two intermediate dilutions) on weight basis. By considering the uncertainty in mass determination by balance as 0.0002 g, the relative combined uncertainty due to dilution,$u_{5,}$ is 0.009%.

The relative combined uncertainty in standard preparation is 0.295%

ii. Uncertainty in sample preparation:

a. Mass of the sample: Approximately 200 mg of solid sample aliquot is taken for each analysis. The relative uncertainty in measurement of sample mass, u_6 is $\frac{0.2 \times 100}{200} = 0.100\%$

b. Final dilution of sample: The uncertainty stated by the manufacturer for 10 mL quartz volumetric flask is 0.1 mL at 95% confidence level. Hence the uncertainty at 1σ level, $u_{7,}$ is 0.500%.

The relative combined uncertainty in sample preparation is 0.510%.

iii. Uncertainty in absorbance measurement:

a. Blank absorbance: To determine the standard uncertainty in blank absorbance, ten independent blank solutions were prepared and absorbance was measured with respect to water. The mean value of blank absorbance is found to be 0.24658 with standard deviation (σ_{blank}) of 0.00526. This uncertainty will take care of minor variations (uncertainties) arising due to variation of mass addition of various reagents like HCl, H_2O_2, H_2SO_4, Curcumin, DMF and small variations in absorbance due to drift in wavelength**.**

b. Absorbance of sample: To arrive at this uncertainty, absorbance of a particular sample with respect to water solution was measured ten times and found a mean absorbance of 0.62154 with standard deviation (σ_{sam}) of 0.00035.

Therefore, standard uncertainty in measurement of absorbance is $\sqrt{\sigma_{blank}^2 + \sigma_{sample}^2}$ = 0.005. Hence the relative standard uncertainty in measurement of absorbance of sample is

$$\frac{0.005 \times 100}{0.62154 - 0.24658} = 1.406\%$$

The uncertainty arising in the absorbance measurement due to the interference of other elements is neglected since boron is selectively extracted [13] from solution**.**

iv. Uncertainty in the slope of calibration plot: Calibration plot was plotted using Origin 6.0 software developed by Origin Lab Massachusetts, USA. This program was used to determine the slope of calibration plot. The slope of calibration plot is 0.00131 with standard error of 0.00001086 Hence u_{10}, relative uncertainty in slope of calibration plot is

$$\frac{0.00001086 \times 100}{0.00131} = 0.824\%$$

v. Recovery of B in measurement: Since no matrix matched certified reference material for boron is available to evaluate the uncertainty in the recovery of measurement, boron was determined in ten independent aliquots of standard boric acid solution. The mean of recovery of 96% was observed. Hence the standard relative uncertainty of recovery, $u_{12} = 4.0\%$.

vi. Reproducibility of the measurement: Boron was determined in six independent solid sample aliquots taken from same lot and found that mean of boron concentration is 1.21 with 3.306 % as relative standard deviation at 1 σ level. The standard relative uncertainty for repeatability is therefore given as $u_{11} = 3.306$ %.

vii. Calculation of expanded uncertainty: Numerical values of variables, uncertainties with their classifications and their conversion to the relative standard uncertainties are summarized in table 3.5. Combined uncertainty (relative) is calculated employing error propagation formula and it is found to be 5.47%. The expanded uncertainty at 95% confidence level is 10.94% (coverage factor 2). The boron concentration for a typical sample was 1.21 $\mu g\ g^{-1}$ and the associated expanded uncertainty amounted to 0.13 $\mu g\ g^{-1}$ at 95 % confidence level. The main sources of uncertainty in the measurement are repeatability, recovery and absorbance measurement.

Table 3.5. Uncertainty components of the boron determination in ammonium diuranate sample with the relative standard deviations.

S.No.	Source of uncertainty	Type	Value of variable	Uncertainty		
				Standard (1 σ)	% Relative Standard	% Each Category (1 σ)
Preparation Of standard (u_{std})						**0.295**
u_1	Purity of Standard Boric acid	B	99.5	0.28868	0.290	
u_2	Weight determination of standard, mg	B	538.8	0.2	0.037	
u_3	Molecular weight of boric acid	B	61.83302	0.0040516	0.007	
u_4	Atomic weight of boron	B	10.811	0.00404	0.037	
u_5	Dilution of stock solution to working standard solution	B	1	0.0000937	0.009	
Preparation of Sample (u_{sam})						**0.510**
u_6	Weight determination of Sample, mg	B	200	0.2	0.100	
u_7	Volume of final solution	B	10	0.05	0.500	
Measurement of absorbance (u_{abs})						**1.406**
u_8	Variation in blank absorbance	A	0.24568	0.00526	--	
u_9	Absorbance of sample	A	0.37496	0.00035	--	
Slope of calibration plot (u_{cal})						**0.824**
μ_{10}	Slope of calibration pot	B	0.00131	0.0000108	0.824	
Recovery (u_{rec})						**4.000**
u_{11}	Recovery	A	100	2.000	2.000	
Repeatability (u_{rep})						**3.306**
U_{12}	Repeatability	A	1.13	0.04	3.540	
Total relative combined uncertainty (1 σ level)						**5.471**

3.1.4. Conclusions

1. In the present method, extraction of boron - curcumin complex with MIBK is avoided as employed by Betty and Day [96]. It should be mentioned that Betty and Day [96] attributed higher blank levels to the use of MIBK.

2. Two diluents namely ethyl alcohol and DMF were assessed. At lower dilutions, DMF gave less blank value with better precision, due to its higher basicity.

3. Interference of nitric acid in the measurement due to its coextraction along with boron has been investigated in detail. Its interference was eliminated by back extraction of HNO_3 with acidified water (0.5 M HCl). These studies will have significant contribution to determine boron in nuclear materials like thorium and plutonium related fuels, which are generally dissolved in HNO_3.

4. There was no significant interference with Al, Cr, Mg, Ca, Fe, Mn, Mo, F^- and W in boron determination.

5. No interference due to the presence of EHD was observed contrary to the earlier work, at the colour development stage with curcumin.

6. Employing the present method boron in ammonium diuranate having concentration less than 1 μg of B/g of U could be determined by taking 200 mg sample, while Betty and Day [96] have taken about 2.5 g of sample at the same boron concentration.

7. There was no loss of boron during the conversion of ADU to U_3O_8.

8. The expanded uncertainty in measurement at 95 % confidence level is 10.94%.

Part II: Determination of Boron in Uranium-Aluminum-Silicon Alloy

3.2.1. Introduction

With the advent of new generation reactors, extensive work has been carried out in developing different type of nuclear fuels, to meet the needs. Uranium-aluminum alloy is used in thermal reactors, test reactors and in nuclear submarines. A small amount of silicon is also added in the uranium-aluminum alloy to improve the metallurgical properties. Boron is one of the stringent specifications in all-nuclear materials because of its high thermal neutron absorption cross section. Hence, it has to be determined accurately in all the nuclear materials including U-Al-Si alloy.

Puphal et al. [110] determined boron content, in percentage level, in uranium – aluminum alloy samples by spectrophotometry with carminic acid after dissolving in HCl and H_2O_2. Hamner and Deaeth [111] determined boron in silicon bearing alloys by pyrohydrolysis separation of boron at 1473 K and its quantification employing Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Makishima et al. [112] and Orazio [113] determined boron in silicate rocks by Inductively Coupled Plasma Mass spectrometry (ICP-MS), after decomposition of the sample with HF in the presence of mannitol. Parashar et al. [114] determined boron in high purity silicon material by spectrophotometry with curcumin as a complexing agent after dissolving the sample in a mixture of concentrated HF, HNO_3 and 0.1% of mannitol. However, significant variation in the boron values was reported. Taddia et al. [115] determined boron content in silicon doped (max 56 $\mu g\ g^{-1}$) gallium arsenide. In their methodology, after dissolving the sample in aquaregia, boron was separated from the matrix employing 2-ethyl hexane 1,3 diol (EHD) in choloroform. After removing interfering species from separated organic phase by treating with dilute HCl, boron was determined by spectrophotometry with curcumin. The detection limit of the method is 0.6 $\mu g.\ g^{-1}$ and relative standard deviation in the determination of boron (precision) is ±20% at 95% confidence level.

During the present studies, efforts to dissolve the uranium-aluminum-silicon sample with aquaregia were futile. This may be due to higher amounts of silicon (~ 36 $mg.\ g^{-1}$) in the sample. No published literature is available, to our knowledge, for the determination of boron content in uranium-aluminum-silicon alloy samples. In the present studies, efforts are made to develop a methodology for the determination of boron in U-Al-Si alloy samples employing spectrophotometry with curcumin as a complexing agent. To determine boron content by spectrophotometry with curcumin, the sample has to be either dissolved quantitatively without loss of boron or boron has to be leached quantitatively. Further, to overcome the interferences from water and other interfering ions, boron has to be separated from the solution preferably employing solvent extraction. It is well known that HF interferes in the spectrophotometric determination of boron with curcumin since it will form strong complex with boron (BF_3 or BF_4^-) [86]. As mentioned in part I of this chapter, it is also observed that HNO_3 above 1.0 M interferes in the determination of boron with curcumin [116]. Hence, present investigations have been aimed at developing a methodology employing spectrophotometry for the determination of boron in U-Al-Si alloy without using these interfering acids.

3.2.2. Experimental

3.2.2.1. Reagents

All the reagents used were of A.R. grade. High purity water obtained from Milli-Q Academic apparatus (Billerica, MA, USA) was used for all the dilutions/preparations of samples. Standard boric acid stock solution (96.6448 g) of 974.75 µg g^{-1} was prepared by weight method by dissolving 0.5388 g of G.R. grade boric acid taken in polypropylene volumetric flask with water. The final working standard solution of 0.5957 µg g^{-1} of boron was made by diluting above stock solution appropriately (118.082 and 11.257 µg g^{-1} as intermediates). Quartz or polypropylene ware was used to avoid contamination of boron from glassware.

3.2.2.2. Procedure

About 200 mg of sample (U-Al-Si alloy granules) was taken in 20 mL quartz weighing bottle. Immediately after the addition of 1.0 mL of 6 M HCl solution, the weighing bottle was closed with leak tight quartz stopper (to avoid the loss of boron by evaporation) and kept in water bath for 5 minutes to bring it to room temperature (25 ºC). To sustain the internal pressure due to release of gases, the lid and vessel were held tightly by means of metallic springs. Another portion of 3.0 mL of the acid solution (6 M HCl) was added and the bottle cooled to room temperature. Acid was added in two steps since single step addition of acid leads to vigorous reaction. After cooling to room temperature, 1.0 mL of 30% H_2O_2 was added to the contents, the bottle was stoppered and heated to ~80 ºC in water bath for 10 minutes to destroy the excess of H_2O_2 and to facilitate the dissolution of the sample to the maximum possible extent (about 90% of sample was dissolved) and also preventing loss of boron during heating (since boric acid is highly steam volatile). After cooling to room temperature, the stopper was removed and washed. The entire solution was quantitatively transferred to a quartz centrifuge tube using 1.0 mL of water. The solution was centrifuged at around 1300 rotation per minute (rpm) for 5 minutes to settle the undissolved material. The supernatant solution was separated and the undissolved material (about 20 mg i.e. 10% of the sample) was washed with 1.0 mL of water, centrifuged and the supernatant liquid was added to the earlier separated solution.

To the separated and clear supernatant solution, 1.0 mL of 10% 2- ethyl hexane 1,3 diol (EHD) in $CHCl_3$ was added and stirred for 3 minutes with magnetic stirrer. The two phases were allowed to settle and the organic phase was separated by suction using polypropylene weight burette. This process was repeated for five times for quantitative separation of boron, i.e. boron was separated by batch extraction. From the entire organic phase thus collected, $CHCl_3$ was evaporated in a fume hood, either by heating on water bath (~80 ºC) or natural evaporation at room temperature by keeping overnight. 1.0 mL of 0.375% curcumin in CH_3COOH and 0.5 mL of concentrated H_2SO_4 were then added to the extract left after evaporation of $CHCl_3$. After about 40 minutes, this mixture was transferred into a 10 mL standard quartz volumetric flask and diluted with N, N-dimethyl formamide (DMF), for deprotonation of protonated curcumin. Blank solution was prepared in an identical manner by taking same amounts of all the reagents without the sample and following identical steps excepting centrifugation. The absorbance of the coloured complex of the sample was measured at 550 nm with reference to blank solution by using quartz cell having 1 cm path length.

3.2.3. Results and Discussion

3.2.3.1. Quantitative extraction of boron

Detailed investigations on extraction of boron with 10% EHD in $CHCl_3$ from standard boric acid aliquot solutions showed that eighty percent of boron is extracted in each batch extraction and hence four batch extractions were adequate for quantitative recovery of boron. Details about time required for quantitative complex formation between curcumin and boron under the experimental conditions; effect of different diluents viz. ethyl alcohol and DMF; interference studies with different cation and anions and effect of different acid media have been discussed earlier.

3.2.3.2. Calibration plot

By analyzing standard boric acid (0.5957 $\mu g\ g^{-1}B$) aliquots employing above procedure, except centrifugation, calibration plot between absorbance and total amount of boron present in

10 mL solution i.e., total amount of B present in aliquot was plotted. A linear regression equation attained as

$$A= 0.00138 \times w - 0.01408 \ldots\ldots\ldots(3)$$

Where

A = Absorbance

w = Amount of boron present aliquot in ng.

The linear correlation coefficient is 0.9926 over the linear range of 80 – 730 ng with eight data pair points.

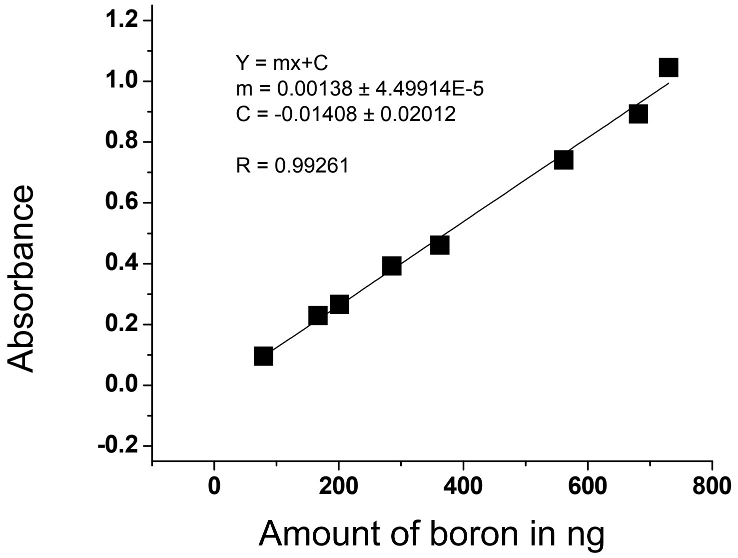


Fig.3.4. Calibration plot for boron.

3.2.3.3. Precision and detection limit of the method

Ten independent standard boric acid aliquots were extracted and analyzed with relative standard deviation (R.S.D) of ±3.0 % (precision at 1σ level) and 98% mean of recovery was achieved. The calibration plot was checked for its reproducibility by analyzing standard boric acid aliquots at different time intervals and found that even after 6 months, same R.S.D. i.e., 3.0% was obtained. Ten independent blank solutions were prepared employing the procedure as mentioned for the sample and absorbance was measured with respect to water. The standard deviation (σ) in absorbance measurement was 0.00526. The absolute limit of detection [103] of this method as evaluated employing calibration plot (3σ/ slope of calibration plot) was found to be 14 ng (0.07 μg g^{-1} at sample size of 0.2000 g).

3.2.3.4. Standardization of the method

The method has been evaluated by standard addition method. Standard boric acid aliquot was added (B_{added}) to the solid sample aliquot and then total boron (B_{total}) was determined as described in experimental section. Boron in the sample was calculated as

$$B_{sample} = B_{total} - B_{added} \qquad (4)$$

Typical results on the analysis of boron for the method standardization are given in table 3.6. Results obtained by both the methods i.e. direct and standard addition methods, agreed well within ± 3%.

Table 3.6. Standardization of the method by standard addition method.

Sample	Amount of sample (g)	Amount of standard boron added (ng) B_{added}	Total Amount of boron measured (ng) B_{total}	Amount of boron in sample (ng) $B_{sample} = B_{total} - B_{added}$	Conc. Of boron in sample (μg g^{-1})
U-Al-Si -01	0.2223	297.7	426.4	128.7	0.45
U-Al-Si -01	0.2170	0.0	236.2	236.2	0.45
U-Al-Si -02	0.1558	143.2	405.2	262.0	1.68
U-Al-Si-02	0.1789	0.0	304.5	304.5	1.70
U-Al-Si -03	0.1670	343.6	475.0	131.4	0.79
U-Al-Si -03	0.2281	0.0	182.1	182.1	0.80

3.2.3.5. Validation of the method

The method has been validated using an independent method by dissolving the sample by acid digestion in a mixture of HF and HNO_3 in the presence of mannitol and determining boron employing inductively coupled plasma – atomic emission spectroscopy (ICP-AES) [117]. The results obtained in the determination of boron from U-Al-Si alloy employing both the methods are given in table 3.7. It can be seen that by applying statistical treatment of the data (t test), there is no significant difference (at 95% confidence interval) between the two methods. As mentioned in the Introduction Section, since HF interferes in the quantitative extraction of boron with EHD, the quantitative dissolution of the sample in presence of HF was not employed in the present methodology.

Table 3.7. Validation of the method.

Sample name	Present method[a] Concentration of Boron (µg g^{-1})	ICP-AES[b] Concentration of Boron (µg g^{-1})
U-Al-Si-04	0.39 ± 0.01	0.40 ± 0.10
U-Al-Si-05	1.05 ± 0.03	1.10 ± 0.20

[a]Mean of five determinations with standard deviation

[b]Mean of five determinations with standard deviation

Table 3.8. Determination of boron in samples.

Sample ID	Amount of sample (g)	Amount of B Obtained (ng)	Conc. Of B (µg/g)
SILUMIN-02	0.2730	131.6	0.482
SILUMIN-03	0.1998	173.0	0.866
U-Al-Si-02	0.1558	286.2	1.837
U-Al-Si-03	0.1020	225.4	2.210

3.2.3.6. Contamination of boron from reagents

The contamination of boron from various reagents (EHD, $CHCl_3$, HCl, H_2O_2, DMF, CH_3COOH, H_2SO_4 and high purity water) employed in the methodology could vary from batch to batch. Since same amounts of the reagents were taken from same batch for blank as well as for the sample, and the absorbance of the sample is measured against the blank, it is not necessary to determine boron contamination from these reagents separately as it would not affect the results.

3.2.3.7. Application

After establishing the methodology for the determination of boron in U-Al-Si alloy, several samples were analysed. Also the present method was extended to determine boron content in silicon-aluminum-nickel alloys samples. Few results are given in table 3.8.

3.2.3.8. Calculation of combined and Expanded Uncertainty in measurement

The uncertainty in the each step of measurements was calculated following the procedure as given in earlier part. Numerical values of variables, uncertainties with their classifications and their conversion to the relative standard uncertainties are summarized in table 3.9. Combined uncertainty (relative) is calculated employing error propagation formula and it is found to be 4.420%. The expanded uncertainty at 95% confidence level is 8.840% (coverage factor 2). The boron concentration for a typical sample was 1.13 μg g^{-1} and the associated expanded uncertainty amounted to 0.10 μg g^{-1} at 95 % confidence level. The main sources of uncertainty in the measurement are repeatability, recovery and absorbance measurement.

3.2.4. Conclusion

Boron concentration has been determined in U-Ai-Si alloy samples without using hydrofluoric acid and nitric acid.Boron content has been determined at levels less than 0.5 μg g^{-1}, in 200 mg sample (quantification limit of the method is 0.2 μg g^{-1}). Relative standard deviation of the method at 1 σ level is 3.0%. The expanded uncertainty in measurement at 95% confidence level is 8.840%. The estimates of the expanded uncertainty give confidence and thus demonstrate the fitness of the methodology developed. The present method could be employed for the determination of boron in silicon related nuclear reactor materials like Silicon-Aluminum-Nickel alloy (SILUMIN) and Uranium – Silicon alloy.

Table 3.9. Uncertainty components of the boron determination in U-Al-Si alloy sample with the relative standard deviations.

S.No	Source of uncertainty	Type of uncertainty	Value of variable	Standard Uncertainty (1 σ)	(%) Relative Standard Uncertainty (1 σ)	(%) Each Category Uncertainty (1 σ)
Preparation Of standard (u_{std})						**0.295**
u_1	Purity of Standard Boric acid	B	99.5	0.28868	0.290	
u_2	Weight determination of standard, mg	B	538.8	0.2	0.037	
u_3	Molecular weight of boric acid	B	61.83302	0.0040516	0.007	
u_4	Atomic weight of boron	B	10.811	0.00404	0.037	
u_5	Dilution of stock solution to working standard solution	B	1	0.0000937	0.009	
Preparation of Sample (u_{sam})						**0.510**
u_6	Weight determination of Sample, mg	B	200	0.2	0.100	
u_7	Volume of final solution	B	10	0.05	0.500	
Measurement of absorbance (u_{abs})						**1.406**
u_8	Variation in blank absorbance	A	0.24568	0.00526	--	
u_9	Absorbance of sample	A	0.37496	0.00035	--	
Slope of calibration plot (u_{cal})						**0.824**
u_{10}	Slope of calibration pot	B	0.00138	0.0000108	0.824	
Recovery (u_{rec})						**2.000**
u_{11}	Recovery	A	100	2.000	2.000	
Repeatability (u_{rep})						**3.540**
u_{12}	Repeatability	A	1.13	0.04	3.540	
Total relative combined uncertainty (1 σ level)						**4.420**

Part III: Determination of boron in Zirconium – Niobium alloy

3.3.1. Introduction

Zirconium alloys are extensively used as construction materials in nuclear power reactors for various purposes e.g. as cladding, coolant channels etc. because of their adequate aqueous corrosion resistance, low neutron absorption cross section, good elevated temperature mechanical properties and irradiation stability. Boron doped zirconium – niobium alloy rods are used as neutron reactivity control rods in advanced nuclear reactors. In addition to the boron content, information about its distribution over the entire length of the rod is also essential for neutron reactivity calculations. This calls for the precise and accurate determination of boron, in such matrices. Several methodologies like ICP-AES [118], ICP-MS [119], GD-MS [120], DC arc AES [121,122] and spectrophotometry [123, 124] are reported in the literature for the determination of boron from zirconium and its alloy materials. Because of simplicity, comparable sensitivity with other methods, non-requirement of sophisticated equipment and less operating cost, spectrophotometic methods are preferable compared to other methods. It may be mentioned that, in all the instrumental methods viz., ICP-AES, ICP-MS, GD-MS, DC arc AES, matrix matched standards are necessary for analysis. However in the spectrophotometric method, matrix matched standards are not a necessary requirement once the method is validated for the determination of boron from any matrix.

Hayes and Metcalfe [123] determined boron content in zirconium materials by spectrophotometry with curcumin as a complexing agent. In this method, sample was dissolved in concentrated H_2SO_4 and $NH_4(SO_4)_2$ mixture and the resultant clear solution was diluted with concentrated H_2SO_4. From this about 2.5mL solution was aliquoted and colour was developed with curcumin. Boron - curcumin complex was precipitated by the addition of water. Precipitated complex was separated by filtration and then re-dissolved in ethyl alcohol. Absorbance of the resultant solution was measured at 550 nm. About 20% deviation in the results was reported. Furthermore, tin, an alloying element in zircaloy, was reported to interfere in this methodology. To avoid interference from tin, these authors employed elaborate and tedious column separations before absorbance measurement.

In Freegarde and Cartwright [124] methodology for determination of boron in zirconium, the sample was dissolved using bromine water and methanol mixture. Excess bromine water was destroyed with stannous chloride. Boron was determined by spectrophotometry employing curcumin after the separation of boron as methyl borate ester by distillation.

However, efforts to dissolve zirconium – niobium sample with bromine water and methanol mixture were futile, which may be due to presence of niobium.

Present investigations aimed at adopting the H_2SO_4 and $NH_4(SO_4)_2$ dissolution method to dissolve Zr-Nb alloy for determining boron. With a view to improving the accuracy in measurements, a separation step for boron from the solution was introduced.

3.3.2. Experimental

3.3.2.1. Reagents

All the reagents used were of A.R. grade. High purity water obtained from Milli-Q Academic apparatus (Billerica, MA, USA) was used for all the dilutions/preparations of samples. Standard boric acid stock solution (96.6448 g) of 974.75 µg g^{-1} was prepared by weight method by dissolving 0.5388 g of G.R. grade boric acid taken in polypropylene volumetric flask with water. The final working standard solution containing 0.706 µg g^{-1} of boron was made by diluting this stock solution appropriately (104.254 and 9.857 µg g^{-1} as intermediates). Quartz or polypropylene ware was used to avoid contamination of boron from glassware.

3.3.2.2. Procedure

i. Sample dissolution: About 50 mg of zirconium – niobium sample in the form of turnings was taken in a100 mL quartz round bottom flask. 1.0 g of ammonium sulphate and 5.0 mL of concentrated sulphuric acid were added. Immediately after the addition of the acid, the flask was connected to a water-cooled condenser. The outlet end of condenser was dipped in de-ionized water to trap the gaseous products. The apparatus employed for the dissolution is shown in the figure 3.5. The flask containing the sample and the dissolution mixture was heated with the help of heating mantel until clear solution was formed. After cooling the solution to room temperature, the solution in the flask and the condensate were transferred quantitatively to a pre-weighed polypropylene 100 mL flask with de-ionised water. A reagent blank solution was also prepared in the same way by adding all the reagents excepting sample.

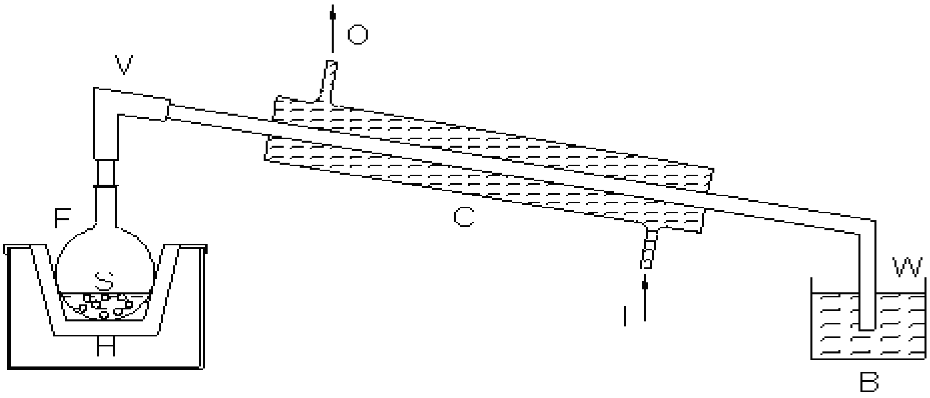


Fig.3.5. Dissolution setup.

(H: heating mantle, S: sample along with reagents mixture, F: round bottom quartz flask, V: quartz v type connector, C: Water cooled condenser, I: inlet of water for condenser, O: outlet of water for condenser, W: water for trapping the uncondensed gaseous products, B: quartz beaker)

ii. Separation of boron: A weighed aliquot of the sample solution (about 0.5 g) was taken in a 10 mL quartz beaker and to it 3.0 mL de-ionised water was added. 1.0 mL of 10% 2- ethyl hexane 1,3 diol (EHD) in $CHCl_3$ was added to the above solution. The mixture was stirred for three minutes using a magnetic stirrer, to facilitate the extraction of boron into the organic phase. The two phases were allowed to settle and the organic phase was separated by suction using a polypropylene weight burette. This process was repeated four times (four batch extractions) for quantitative separation of boron. The organic phase separated in each extraction was collected and pooled in another quartz beaker.

iii. Colour development and absorbance measurement: The $CHCl_3$ was evaporated from the entire organic phase, in a fume hood, either by heating on water bath (~80 ºC) or natural evaporation at room temperature by keeping overnight. 1.0 mL of 0.375% curcumin in CH_3COOH and 0.5 mL of concentrated H_2SO_4 were then added to the residue left subsequent to evaporation of $CHCl_3$. After about 50 minutes, this mixture was quantitatively transferred into a 10 mL standard quartz volumetric flask and diluted with N, N-dimethyl formamide (DMF), for deprotonation of protonated curcumin. The blank for absorbance measurement was also prepared in the same way by taking reagent blank solution instead of sample solution. The absorbance of the coloured complex with reference to blank solution was measured at 550 nm by using quartz cell having 1 cm path length.

3.3.2.3. Calibration plot

Known amounts of standard boric acid aliquots were taken and 0.5 mL (~ 0.5 g) of reagent blank solution was added to each aliquot. The solution was made upto 3.5 mL with deionised water. Boron was separated and colour was developed with curcumin employing the procedure given above. A linear calibration plot was constructed between amount of boron in aliquot and respective absorbance of solution.

3.3.3. Results and Discussion

3.3.3.1. Sample dissolution

Dissolution step is very critical and to a large extent decides the final results. During the initial stages of experiment, attempts to dissolve the sample in ammonium sulphate and sulphuric acid mixture taken in an open beaker and by heating directly on a hot plate, around 40 – 50 % loss of boron due to volatilization was observed. To overcome the loss of boron due to volatilization, the sample along with $(NH_4)_2SO_4$ and H_2SO_4 was taken in a quartz round bottom flask and closed with a spring-loaded stopper. However, there was rigorous bumping of the solution due to water drops condensed on the cooler parts of the flask falling back into the hot solution. It was also observed that even after heating for an hour, sample was not dissolved quantitatively. To avoid the loss of boron and prevent bumping of solution due to the water droplets falling into the hot sulphuric acid, the above set up has been modified. A water-cooled condenser was attached to the flask, instead of the stopper. The condenser allows the escape of water vapour. The boric acid carried away by this vapour was condensed / trapped by dipping the outlet of the condenser in de-ionised water. Within five minutes sample was dissolved and a clear solution was obtained.

3.3.3.2. Quantitative extraction of boron and complexation with curcumin

Preliminary studies on standard boric acid aliquot solutions showed that three batch extractions with 10% EHD in $CHCl_3$ were adequate for quantitative recovery of boron. Hence, in all further experiments, extraction was carried out four times. It was found that 40 minutes was required for quantitative complex formation between curcumin and boron in EHD. As mentioned in part I of this chapter, no interference from ions, Al, Cr, Mg, Ca, Fe, Mn, Mo, F^-, W even at presence of 1000 times to the amount of boron present in aliquot. Studies carried out on the determination of boron in presence of tin showed that there is no interference with tin in present methodology which may be due to selective separation of boron with EHD.

3.3.3.3. Calibration plot, Precision and detection limit of the method

The calibration plot obtained in the present method is shown in figure 3.6. A linear regression was carried out on the calibration plot. Absorbance and the amount of boron present in the sample are related by the equation

$A = 1.3879 \times w$ (5)

Where

A = Absorbance

w = Amount of boron present aliquot in μg.

The linear correlation coefficient is 0.9994 over the linear range of 0.1 – 0.8 μg with eight data pair points.

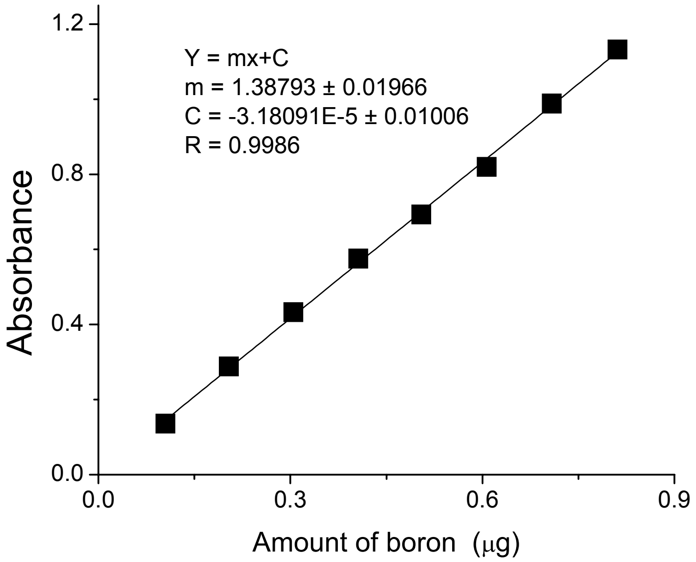


Fig.3.6. Calibration plot for boron.

Relative standard deviation (RSD) and mean recovery of boron in ten independent standard boric acid aliquots were ±3.0 % (precision at 1σ level) and 98% respectively. The calibration plot was checked for its reproducibility by analyzing standard boric acid aliquots at different time intervals over a three month period and there was no deviation in the statistics. From a given sample, four independent solid aliquots were taken, dissolved and boron was determined in each of the dissolved solid aliquots in duplicate (total 8 determinations.) A relative standard deviation of 3.33% was attained. This is in contrast to about 14% reported by Hayes and Metcalfe [124]. The improvement, both in terms of RSD and recovery obtained in the present work is possibly due to prevention of loss of boron during dissolution of sample and also quantitative and selective separation of boron with EHD prior to its complexation with curcumin for spectrophotometry. In order to determine the limit of detection, ten independent blank solutions were prepared and absorbance was measured with respect to water. The standard deviation (σ) in absorbance measurement was 0.00556. The absolute limit of detection [20] of this method has been evaluated employing the relation 3σ/ slope of calibration plot and found to be 0.012 µg (0.048 wt% for an aliquot of 0.5 mL from 100 mL solution at sample size of 50 mg).

3.3.3.4. Evaluation of the method

The method has been evaluated by standard addition method. Standard boric acid aliquot was added (B_{added}) to the solid sample aliquot and then total boron (B_{total}) was determined as described in experimental section. Boron in the sample was calculated as

$$B_{sample} = B_{total} - B_{added} \qquad (6)$$

Typical results on the analysis of boron for the standardization of the methodology are given in table 3.10. Results obtained by both the methods i.e. direct and standard addition methods, agreed well within ± 4%.

Table 3.10. Evaluation of the method by standard addition method.

Sample ID	Concentration of boron (wt%)	
	Direct method	Standard Addition method
Zr - 01	0.215	0.212
Zr - 02	0.232	0.224
Zr – 03	0.384	0.379
Zr - 04	0.372	0.383

3.3.3.5. Validation of the method

The method has been validated by an independent method, where in sample was dissolved in a mixture of HNO_3 and HF in the presence of mannitol and boron was determined by inductively coupled plasma atomic emission spectroscopy, ICP-AES [117]. The results are given in table 3.11. It was observed that, by applying statistical treatment to the data (t - test), there is no significant difference (at 95% confidence interval) between the two methods. This acid mixture was not adopted in the spectrophotometry procedure as our earlier studies showed that HNO_3 interferes in the determination of boron with curcumin after its extraction with EHD. Apart from this, in the presence of mannitol, quantitative separation of boron with EHD may not possible.

Table 3.11. Validation of the method.

Sample name	Present method[a] Concentration of Boron (wt%)	ICP-AES[b] Concentration of Boron (wt%)
Zr - 05	0.213 ± 0.008	0.210 ± 0.010
Zr - 06	0.427 ± 0.012	0.420 ± 0.010

[a] Mean of five determinations with standard deviation

[b] Mean of five determinations with standard deviation

3.3.3.6. Application of methodology

After establishing the methodology, the present method is being employed to determine boron content in several zirconium- niobium alloy samples, on routine basis. A few results are given table 3.12.

Table 3.12. Typical results of analysis for boron in Zr- Nb alloy samples.

Sample Id	Amount of sample (g)	Amount of boron obtained (μg)	Conc. of boron (wt%)
Zr- 07	0.0359	66.11	0.218
Zr - 08	0.0396	79.40	0.200
Zr - 09	0.0360	123.80	0.343
Zr - 10	0.0357	143.40	0.402
Zr - 11	0.0592	94.13	0.159
Zr - 12	0.0571	246.12	0.431

3.3.3.7. Calculation of combined and Expanded Uncertainty in measurement

The uncertainty in each step of measurement was calculated following the procedure as given in part I of this chapter. The Combined uncertainty (relative), calculated employing error propagation formula is found to be 4.387%. The expanded uncertainty at 95% confidence level is 8.774% (coverage factor 2, Table 3.13).

3.3.4. Conclusion

Zirconium – Niobium samples were dissolved with ammonium sulphate and sulphuric acid without loss of boron by incorporating water cooled condenser in the system. Boron has been determined in these samples with a precision and accuracy of 3%. The present method has been evaluated with standard addition method and validated by an independent method based on Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP - AES). The present investigation is a significant improvement over the existing methodologies. The method has been employed to determine the boron content in zirconium – niobium samples on regular basis. It could also be employed to determine the ultra trace level of boron in zirconium matrix. For this, after dissolution of the sample, the dilution step is avoided and the acidity of the solution is decreased to less than 6M by adding NaOH, prior to extraction and determination of boron.

Table 3.13. Uncertainty components of the boron determination in Zr-Nb alloy sample with the relative standard deviations.

S.No	Source of uncertainty	Type	Value of variable	Standard Uncertainty (1 σ)		
				Standard	Relative (%)	Category (%)
Preparation Of standard (*u_{std}*)						**0.295**
u_1	Purity of Standard Boric acid	B	99.5	0.28868	0.290	
u_2	Weight of standard, mg	B	538.8	0.2	0.037	
u_3	Molecular weight of boric acid	B	61.83302	0.0040516	0.007	
u_4	Atomic weight of boron	B	10.811	0.00404	0.037	
u_5	Dilution to working standard solution	B	1	0.0000937	0.009	
Preparation of Sample (*u_{sam}*)						**0.642**
u_6	Weight of solid Sample (mg)	B	50	0.2	0.400	
u_7	Weight of total solution, (g)	B	105	0.0002	0.0002	
u_8	Weight of liquid aliquot (mg)	B	500	0.2	0.040	
μ_9	Volume of final solution	B	10	0.05	0.500	
Measurement of absorbance (*u_{abs}*)						**1.277**
μ_{10}	Variation in blank absorbance	A	0.24568	0.00526	--	
μ_{11}	Absorbance of sample	A	0.88553	0.00625	--	
Slope of calibration plot (*u_{cal}*)						**1.416**
u_{12}	Slope of calibration pot	B	1.38793	0.01966	1.416	
Recovery (*u_{rec}*)						**2.000**
μ_{13}	Recovery	A	100	2.000	2.000	
Repeatability (*u_{rep}*)						**3.330**
μ_{14}	Repeatability, wt%	A	0.210	0.007	3.330	
Total relative combined uncertainty (1 σ level)						**4.387**

Chapter IV

Determination of Boron in Zr-Nb Alloy Samples by BF_4^- Ion Selective Electrode

4.1. Introduction

Several methodologies like inductively coupled plasma – atomic emission spectrometry (ICP-AES) [118], inductively coupled plasma – mass spectrometry (ICP-MS) [119], glow discharge- mass spectrometry (GD-MS) [120], direct current arc atomic emission spectrometry (DC arc AES) [121, 122] and spectrophotometry [123, 124] are reported in the literature for the determination of boron in zirconium and its alloy materials. Except spectrophotometry, other techniques require sophisticated instrumentation and high operation cost. Also, it may be mentioned that, in all the instrumental methods viz., ICP-AES, ICP-MS, GD-MS, DC arc AES, matrix matched standards are necessary for analysis. Many times it may not be possible to get matrix matched standards. Even though spectrophotometry is a simple technique it requires elaborate procedures for selective separation of boron and complex formation with suitable reagents. A need therefore exists for a simple, sensitive and fast methodology to determine boron content in zirconium samples on routine basis.

Tetrafluoroborate ion selective electrode (BF_4^- ISE) method is one of the sensitive and fast methods for the determination of boron. Several in-house developed or commercially available BF_4^- ISEs have been employed to determine the boron content in various matrices like water [125-127], silicon [128], glasses [129] and aluminum oxide-boron carbide [130] samples. However, to our best knowledge, no information is available on the determination of boron in zirconium matrix employing BF_4^- ISE. Hence, studies have been carried out to develop BF_4^- ISE methodology for the determination of boron in zirconium-Niobium alloy samples employing commercially available Orion 9305 BF_4^- -ISE.

As mentioned in the previous chapter, any developed methodology before applying for routine analysis, should be statistically treated for estimating the combined and expanded uncertainty in measurement it is able to provide to increase the confidence on measurand values. The present chapter describes in detail (i) the methodology developed for the determination of boron in Zr-Nb alloy samples by potentiometry with BF_4^- ion selective electrode and (ii) estimation of expanded uncertainty as per the ISO guidelines.

4.2. Experimental

4.2.1. Apparatus

A double channel Orion 720A potentiometer was used to measure the potential. Orion 9305 BN tetrafluoroborate ion selective electrode was used to determine boron content. Potential was measured with respect to Orion 9002 Ag/AgCl double junction reference electrode containing 2 M NH_4SO_4 as outer filling solution. Eutech pH electrode was used to measure the pH of the solution.

4.2.2. Reagents

All the reagents used were of analytical reagent (A.R.) grade. High purity water obtained from Milli-Q Academic apparatus (Billerica, MA, USA) was used for all the dilutions/preparations of samples. Standard boric acid stock solution (107.5568 g) with 1007.8 µg g^{-1} of boron content was prepared by dissolving 0.6199 g of guaranteed reagent (G.R.) grade boric acid in a polypropylene volumetric flask with water. This stock solution was diluted suitably to prepare standard boron solution of required concentration. Quartz or polypropylene ware was used to avoid contamination of boron from glassware.

4.2.3. Procedure

About 100 mg of the zirconium - niobium alloy sample was taken in a 50 mL volumetric flask and 5 mL of de-ionised water was added. To it 1 mL of 20% HF was added and immediately the flask was closed with a lid to eliminate the loss of boron as BF_3 if any. The flask was kept in a water bath maintained at 60 ºC for 2 h. After cooling to room temperature, 900 µL of ~ 7 M NH_4OH was added and then diluted to about 40 mL. The solution was then transferred to a 100 mL polyvinyl chloride (PVC) beaker. The pH of the solution was adjusted to about 5 employing 0.1 M and 0.001 M NH_4OH. The solution was then quantitatively transferred to a 50 mL volumetric flask and made up to the mark with de- ionised water. The solution was finally transferred to a 100 mL PVC beaker. Potential was measured employing BF_4^- ion selective electrode with respect to the Ag/AgCl reference electrode.

4.2.4. Calibration

Standard boric acid aliquots were taken and by employing the procedure mentioned above, boron is quantitatively converted to BF_4^-. Potential was measured using BF_4^- ISE and the calibration plot was constructed between the potential (mV) and logarithm of mass fraction of boron in solution (µg/g). The calibration plot is shown in figure 4.1. Similarly, calibration plot was also obtained employing standard $NaBF_4$ solutions.

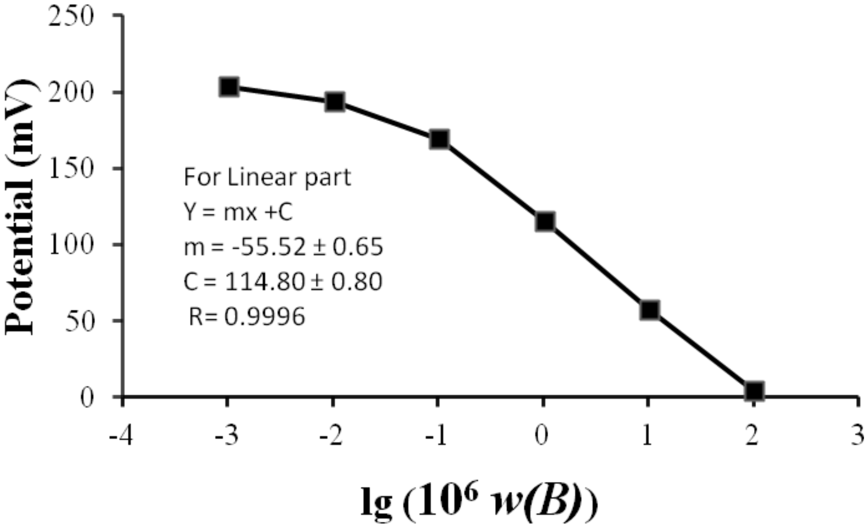


Fig.4.1. Response of the BF_4^- ion selective electrode in dependence of mass fraction of boron *w*(B)

4.3. Results and Discussion

4.3.1. Quantitative formation of tetrafluoroborate

One of the critical parameters in the method under discussion is quantitative conversion of boron to tetrafluoroborate as the BF_4^- ISE responds only to the BF_4^- ion. Katagiri et. al [131] reported that at a free fluoride concentration of 1.0 M and pH 0.7-0.8, 96.4% of boron in a form of boric acid was converted to BF_4^- within 20 min at 20 °C. To check the quantitative conversion of boron in Zr-matrix into BF_4^-, different amounts (up to 6mL) of 1.6 M HF were added, maintained at ambient temperature (25 °C) by keeping in water bath and the boron mass fraction, as BF_4^-, measured periodically. It was observed that even after 24 h only 50 % of the boron was converted to BF_4^-. It was necessary to heat the solution for complete conversion of boron into BF_4^- ion. After the addition of HF to the sample and when the mixture was kept in the water bath maintained at 60 ºC for 2 h, quantitative conversion of boron to BF_4^- from this matrix was observed.

4.3.2. Calibration plot

From Fig.1, it can be seen that, response is **Nernstian** from 0.1 µg/g to 100.0 µg/g of boron with **Nernstian** slope of -55.5 mV per one order change in mass fraction of boron (µg/g). The calibration plot using $NaBF_4$ also gave similar slope and detection limit.

4.3.3. Effect of pH

To evaluate the effect of pH on the response of ISE, aliquots of $NaBF_4$ (5.0 mL of 102.04 µg/g of B) solutions were taken. After adjusting the pH to a single precise value in the range 1–11 by the addition of dilute NH_4OH and HF, these are diluted to 50 mL. The potential was then measured with BF_4^- ISE. Figure 4.2 shows the measured potential as a function of pH. It can be seen from the figure that the response of ISE is constant over the pH range 3 to 9. The increase in the potential at higher pH may be due to hydrolysis of BF_4^- ion. The decrease in the potential at lower pH may be due to failure of **Donnan** membrane equilibrium [132].

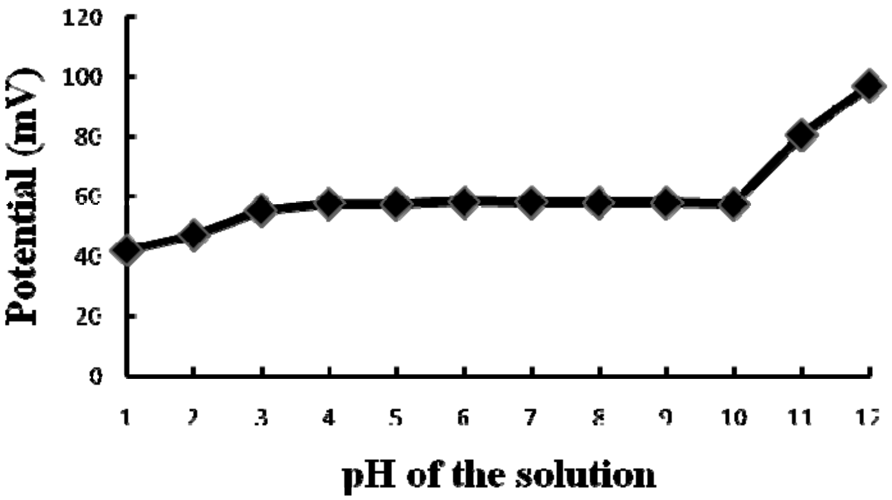


Fig.4.2. Response of BF_4^- ISE at various pH of the solution.

4.3.4. Verification of the method

The developed method has been verified by the standard addition method. Standard boric acid aliquot was added (B_{added}) to the solid sample aliquot and then total boron (B_{total}) was determined as described in the Experimental Section. The boron content in the sample was calculated as $m(B)_{sample} = m(B)_{total} - m(B)_{added}$.

Typical results on the analysis of boron are given in table 4.1. Results obtained by both the methods i.e. direct and standard addition methods, agreed well within ± 5%.

Table 4.1. Verification of the method by standard addition method.

Sample ID	Mass fraction of boron (mg/g)	
	Direct method	Standard Addition method
Zr - Nb- 1	2.06	2.08
Zr - Nb- 2	2.21	2.12
Zr - Nb- 3	4.17	4.21
Zr – Nb- 4	3.60	3.55

4.3.5. Validation of the method

Since standard reference materials for boron in zirconium matrix are not available to us, the developed method has been validated by two independent methods namely ICP-AES and spectrophotometry employing curcumin as complexing agent. The results are shown in table 4.2. From the table it can be seen that at 95% confidence level (t - test) there is no significant difference between the results obtained using the present method and the other two methods.

Table 4.2. Validation of the method.

Sample name	Mass fraction of Boron (mg/g)[*]		
	BF_4^-ISE	ICP-AES	Spectrophotometry
Zr-Nb-5	2.05 ± 0.06	2.10 ± 0.10	2.13 ± 0.08
Zr-Nb-6	4.23 ± 0.10	4.20 ± 0.10	4.27 ± 0.12

[*] Mean of five determinations with standard deviation

4.3.6. Application of methodology:

After establishing the methodology, the present method has been employed to determine boron content in several zirconium- niobium alloy samples. A few results are given in table 4.3.

Table 4.3. Typical results of analysis for boron in Zr- Nb alloy samples with BF_4^-ISE.

Sample Id	Size of sample (g)	Mass fraction of boron (mg/g)
Zr-Nb-7	0.1052	2.14
Zr-Nb-8	0.1202	1.96
Zr-Nb-9	0.0905	3.36
Zr-Nb-10	0.1098	3.94
Zr-Nb-11	0.1206	1.56
Zr-Nb-12	0.0889	4.22

4.3.7. Estimation of uncertainty

The mass fraction (µg/g) of boron (w(B)) in the sample was determined as

$$C_{\mathrm{m}} = \frac{10^{[(p-q)/s]} V\rho}{m.f} \qquad \textbf{...........(1)}$$

Where

p denotes the measured potential (mV)

q the intercept of calibration (mV)

s the variation of potential per one order change in mass fraction of boron solution (mV/lg w(B))

V the volume of the solution (mL)

ρ the density of the solution (g/mL)

f the fraction of boron converted to BF_4^- (0.97)

m Mass of the solid sample (g)

Since standard boric acid aliquots were used to construct the calibration plot, the uncertainties associated with the preparation of standard boric acid have to be considered to evaluate the combined uncertainty in the methodology. The combined uncertainty in the measurement result (mass fraction of boron) is categorized into seven parts. They are relative uncertainty in

(i) standard preparation $(u_{\mathrm{r}})_{\mathrm{std}}$,

(ii) sample mass determination $(u_{\mathrm{r}})_{\mathrm{m}}$,

(iii) volume of the sample $(u_{\mathrm{r}})_{\mathrm{v}}$,

(iv) density the sample solution $(u_r)_\rho$,

(v) calculation of boron mass fraction in solution $(u_r)_w$,

(vi) fraction of boron converted to BF_4^- $(u_r)_f$ and

(vii) repeatability of measurements $(u_r)_{rep}$.

The combined uncertainty u_c is given by

$$u_c = w(B)\sqrt{(u_r)_{std}^2 + (u_r)_m^2 + (u_r)_v^2 + (u_r)_\rho^2 + (u_r)_w^2 + (u_r)_f^2 + (u_r)_{rep}^2} \quad \text{.......(2)}$$

where w(B) is mass fraction of boron in sample.

In the present studies, an attempt has made to address the uncertainties arising due to all the seven components mentioned above. The evaluation of uncertainties from different sources is given below:

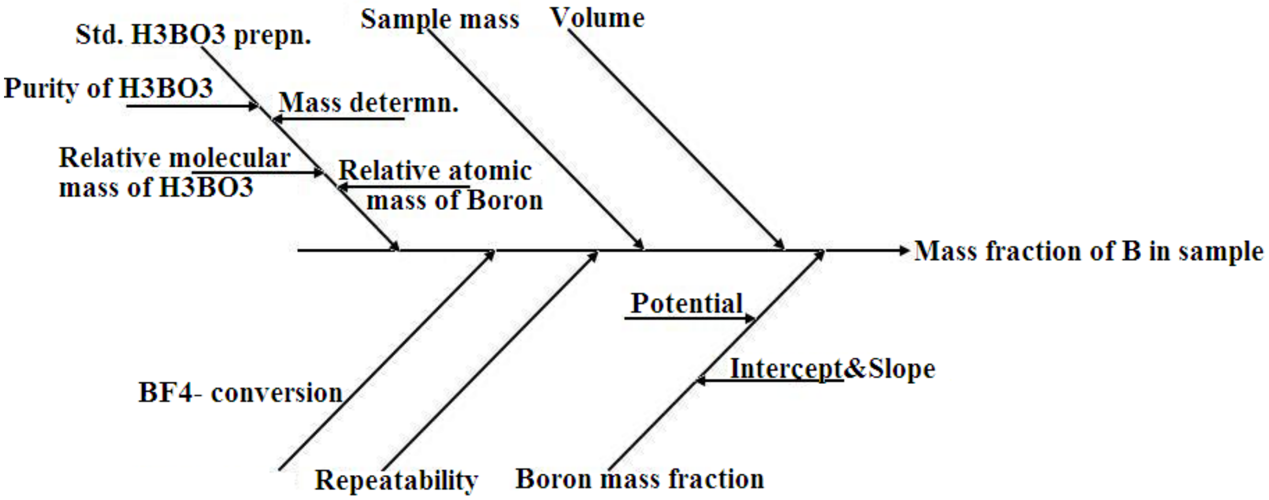


Fig.4.3. Cause effect diagram for estimation of combined uncertainty in determination of boron in Zr-2.5% Nb alloy samples employing BF_4^- ISE.

4.3.7.1. Uncertainty in standard boric acid preparation

i. Purity of ortho boric acid: The manufacturer's certificate mentioned the purity to be (99.5 ± 0.5) %. Assuming a rectangular distribution, the relative uncertainty in the purity is equal to $0.5/\sqrt{3}\ 99.5 = 0.290\%$

ii. Mass determination: As quoted by the manufacturer of the analytical balance used, the uncertainty in mass determination is 0.2 mg over the entire range. Since 619.9 mg of the ortho boric acid was taken for preparation of standard boric acid solution, assuming rectangular distribution, the relative uncertainty involved in determining the mass of the standard is $0.2\,\text{mg}/\sqrt{3}\ 619.9\,\text{mg} = 0.019\%$

iii. Relative Molecular mass of boric acid: The relative molecular mass of boric acid (61.83302) is calculated using relative atomic masses of respective elements. The uncertainty in the relative molecular mass is arrived at considering the individual element atomic masses and their quoted uncertainties as given by IUPAC [109]. Assuming a rectangular distribution the combined uncertainty in the relative molecular mass of boric acid is calculated to be 0.0040516. The relative combined uncertainty in the relative molecular mass of boric acid is 0.0040516/61.83302 = 0.007%.

iv. Relative Atomic mass of boron: Since boron content in the standard solutions is expressed as mass fraction, the uncertainty in relative atomic mass of boron has to be considered. The quoted uncertainty in relative atomic mass of boron by IUPAC [109] is 0.007 and assuming rectangular distribution the uncertainty is 0.00404 and the relative uncertainty in the relative atomic mass of boron is 0.00404/10.811 = 0.037%.

The relative combined uncertainty in standard preparation $(u_\text{r})_\text{std}$ is calculated using the above individual relative uncertainty components to be 0.294%

4.3.7.2. Uncertainty in sample mass determination

Approximately 100 mg of solid sample aliquot is taken for each analysis. The relative uncertainty in measurement of sample mass $(u_\text{r})_\text{m}$, in a typical example is $0.2\,\text{mg}/\sqrt{3}\ 104.2\,\text{mg} = 0.111\%$.

4.3.7.3. Uncertainty in sample volume determination

The uncertainty stated by the manufacturer for the 50.0 mL PVC volumetric flask used in this work is 0.2 mL. Considering triangular distribution, the uncertainty in volume determination is 0.082 mL. Hence the relative uncertainty in volume determination $(u_r)_\text{v}$ is 0.163%.

4.3.7.4. Uncertainty in determination of density of sample solution

The density of five independent sample solutions was determined and the mean of density of sample solution is found to be 1.0008 g/mL with standard deviation of 0.0003 g/mL. Hence relative uncertainty in density determination $(u_\text{r})_\rho$ is $0.0003\,(\text{g/mL})/\sqrt{5}\ 1.0008\,(\text{g/mL}) = 0.0001\%$. This is not considered in the evaluation of combined uncertainty.

4.3.7.5. Uncertainty in calculation of boron mass fraction (µg/g) in solution

i. Measurement of Potential: To determine the standard uncertainty in the measurement of potential, the potential was measured ten times for a particular sample solution. The mean value of the potential is found to be 64.4 mV with a standard deviation of 0.5 mV. Hence standard uncertainty in potential measurement (u_{p}) is 0.158 mV.

ii. Slope and intercept of the calibration plot: Calibration plot was plotted using Origin 6.0 software. This program lists the slope along with standard error employing least square regression method. The slope of the calibration plot is -55.5 (mV/lg w(B)) with standard error of 0.652 (mV/lg w(B)). After employing rectangular distribution, the uncertainty in the slope (u_{S}) is 0.377 (mV/lg w(B)). Similarly, intercept is 114.6 mV with standard error of 0.799 mV. Hence the uncertainty in intercept (u_{C}) is 0.462 mV

The mass fraction of boron in solution is calculated as $w = 10^{(p-q)/S}$ Where

p denotes the measured potential (mV)

q the intercept of calibration (mV)

s the variation of potential per one order change in mass fraction of boron solution (mV/lg w(B))

On taking natural logarithm both the sides and partial differentiation

$$\frac{\partial w}{\partial p} = \frac{w \bullet \ln 10}{s} \qquad \frac{\partial w}{\partial q} = \frac{-w \bullet \ln 10}{s} \qquad \frac{\partial w}{\partial s} = \frac{-w \bullet (p-q) \bullet \ln 10}{s}$$

Substituting these values in the equation for calculation of combined uncertainty in calculation of mass fraction of boron

$$u_w = \sqrt{\left(\frac{\partial w}{\partial p}\mu_p\right)^2 + \left(\frac{\partial w}{\partial q}\mu_q\right)^2 + \left(\frac{\partial w}{\partial s}\mu_s\right)^2} \quad \ldots\ldots. (3)$$

(Note: Here $u_{\mathrm{w}}, u_{\mathrm{p}}, u_{\mathrm{q}}$ and u_{s} are absolute uncertainties) we get

$$\frac{u_w}{w} = \frac{2.303(p-q)}{S}\sqrt{\frac{(u^2{}_p + u_q^2)}{(p-q)^2} + \frac{u_S^2}{(s)^2}} \quad \ldots\ldots\ldots.. (4)$$

After substitution respective values in above equation, relative uncertainty in calculation of mass fraction of boron in solution (µg/g) is 2.471%.

4.3.7.6. Uncertainty in conversion of boron to tetrafluoroborate

In the determination of boron by tetrafluoroborate ion selective electrode, boron has to be converted quantitatively to BF_4^-. Even though conditions are optimized to convert boron to BF_4^-, to the maximum extent possible, but due to chemical reaction equilibrium, traces of un-reacted boron will be invariably present in the solution. As identical conditions are employed for the standard as well as sample solutions, it could be assumed that the extent of formation of BF_4^- will remain same in both the cases. However necessary correction has to be incorporated to arrive at quantitative results. To estimate the uncertainty in fraction of boron converted to BF_4^- ion, boron was determined in five independent aliquots of standard boric acid solution. Average recovery was found to be 97% with standard deviation of 3%. Hence the relative standard uncertainty $(u_r)_f$ is $3/(\sqrt{5}\ \ 97) = 1.383\%$.

4.3.7.7. Repeated measurements

Average mass fraction of boron determined in five independent solid sample aliquots is found to be 4.01 mg/g with standard deviation of 0.14 mg/g. Therefore, the relative standard uncertainty for repeated measurements is $(u_r)_{rep}$ is $0.14\ (mg/g)\ /\ (\sqrt{5}\ \ 4.01\ (mg/g)) = 1.561\%$.

4.3.7.8. Calculation of expanded uncertainty

Numerical values of variables, uncertainties with their classifications and their conversion to the relative standard uncertainties are summarized in table 4.4. The relative combined uncertainty is calculated from all the uncertainty sources indicated above $(u_r)_{std,}$ $(u_r)_{m,}$ $(u_r)_{v,}$ $(u_r)_w$, $(u_r)_f$ and $(u_r)_{rep}$ employing law of uncertainty propagation and found to be 3.25 %. The expanded relative uncertainty is 6.50% (coverage factor 2). The measurement result of the mass fraction of boron in a typical sample is (4.01 ± 0.28) mg/g

4.4. Conclusions

a) The present investigations resulted in the development fast, precise and accurate method for the determination of boron from Zr-Nb matrix.

b) The present method has been evaluated with standard addition method and validated by two independent methods namely ICP – AES and spectrophotometry.

c) Using the analytical methodology developed and employing ISO guidelines, combined relative uncertainty and also expanded relative uncertainty (at coverage factor 2) of measurement were calculated to be 3.25% and 6.50% respectively.

d) The developed method is amenable for routine analysis. To our best knowledge, BF_4^- ISE has been used for first time to determine boron in Zirconium matrix.

Table 4.4. Uncertainty components of the boron determination in Zr-Nb alloy sample employing BF_4^- ISE with the RSD.

Source of uncertainty	*Type*	*Value of quantity*	*Uncertainty Standard*	*Relative Standard uncertainty (%)*	*Each Category Relative uncertainty (%)*
Preparation Of standard (u_{std})					**0.294**
Purity of Standard Boric acid (%)	B	99.500	0.289	0.290	
Mass determination of standard (mg)	B	619.900	0.115	0.019	
Relative molecular mass of boric acid	B	61.8330200	0.0040516	0.007	
Relative atomic mass of boron	B	10.81100	0.00404	0.037	
Mass determination of sample (u_m)					**0.111**
Mass determination of solid Sample (mg)	B	104.200	0.115	0.111	
Volume of the solution (u_v)					**0.163**
Volume of final solution (mL)	B	50.0	0.082	0.163	
Calculation of boron concentration (u_{cal})					**2.471**
Potential measurement (mV)	A	64.4	0.158	--	
Slope of calibration plot (mV/ lg w(B))	B	-55.500	0.377	--	
Intercept of calibration (mV)	B	114.6	0.462	--	
Fraction of conversion of boron to BF_4^- (u_f)					**1.383**
Fraction of conversion of boron to BF_4^- (%)	A	97.000	1.342	1.383	
Repeated measurements (u_{rep})					**1.561**
Repeatability (mg/g)	A	4.010	0.062	1.561	
Relative combined standard uncertainty					**3.253**

Chapter V

Development of ion selective electrode for cesium

5. Importance of Cesium determination in nuclear waste streams

Since nuclear power is an important energy source, many nuclear reactors have been installed throughout the world. The spent fuel from the reactors is reprocessed to recover U and Pu. A lot of radioactive waste is generated in this process [133], the management of which has become an important issue. Cesium and strontium are two important fission products present in this radioactive waste. These are long lived and heat generating radio nuclides ($t_{1/2}$ for ^{137}Cs is 31.2 y and ^{90}Sr is 90 y). It is estimated that the cumulative spent fuel, arising from existing nuclear reactors all over the world, could be around 3.5 x 10^5 tons by the year 2010. In this, the yearly yield for ^{137}Cs alone is estimated to be around 27 MCi [1]. Due to long half life and reasonable thermal output (0.42 W/g), ^{137}Cs has a potential application as the source in gamma irradiators, which are used in environment pollution control, food preservation and sterilization of medical accessories. Due to the toxicity of cesium and its ability to displace potassium from muscles and red cells, removal of cesium from medium and low level nuclear wastes is also desirable. It is thus essential to have knowledge of the amount of cesium in the nuclear waste streams. Removal of ^{137}Cs from nuclear waste facilitates the safe and less expensive methodologies for disposal of high-level waste in deep geological repositories as vitrified waste. Thus its removal from medium and low level nuclear wastes gained importance. Again the extent of removal has to be ascertained by measuring the concentration of Cs.

Radioactivity counting techniques based on gamma spectrometry offer a very sensitive measurement option. However, these involve expensive detection and data analysis systems. Moreover these can be applied only for measuring radioactive cesium. It would be ideal to have a measurement technique, which is reasonably sensitive, easily portable and at the same time can also be applicable to measurement of stable cesium in environment.

One approach that offers rapid, reliable measurements in aqueous environments is the polymeric membrane ion selective electrodes (ISEs). Typically ISEs are composed of a highly selective ionophore incorporated in a ploy vinyl chloride (PVC) matrix, plasticized with suitable plasticizer and a tetraphenylborate type ion exchanger. A diverse range of molecular architectures has been used to design neutral Cs^+- selective ionophores including crown ethers [134, 135], calix[4]arenes [136-140], thiacalix[4]arenes [141, 142], calix[6]arenas [143, 144], zeolite and acetonitrile compounds [145-147]. Calixarene compounds have been widely regarded as important class of macro cyclic host molecules, for the last couple of decades because of their structural and electronic features, which allow a three dimensional control of metal ion complexation, resulting in highly selective and efficient binding properties for specific metal ion. With this in view studies have been carried out to develop ion electrode for cesium employing various calix[4]arene compounds.

<u>Part I:</u> ISE for Cesium with 5-(4′-nitrophenylazo) 25, 27-bis(2-propyloxy)26, 28-dihydroxycalix[4]arene

5.1.1. Introduction

A series of pyridylazo calix[n]arenes including mixed hetroaryl azocalix(n)arenes have been synthesized and reported by Chawla et al. [74]. Preliminary evaluation of synthesized derivatives as molecular receptors for metal ions carried out by these authors indicated that they have good potential to function as selective ionic filters for cesium ions. The synthesized pyridyl azocalix[n]arenes exhibited a red shift of about 50 nm on addition of excess of cesium metal ion with the appearance of a new absorption band near 500 nm accompanied by a profound color change. Other ions did not interfere in such an interaction with cesium. Since no azo calixarene without crown loop has been reported to be used as a selective filter for the cesium encouraged us to investigate further if these compounds could be used as ionophores for measurement of cesium.

In 1994 IUPAC published recommendations for nomenclature of ion selective electrodes [53]. Two methods namely fixed interference method (FIM) and separate solution method (SSM) were recommended for determining selectivity coefficients only when the electrode exhibits a **Nernstian** response to both principal and interfering ion. Later matrix matched potential method was recommended (i) when interfering ions and/or the primary ion do not satisfy the **Nernstian** condition, even if the charges of the primary and interfering ions are equal, (ii) when ions of unequal charge are involved [148]. It should also be mentioned that in recent years, the detection limits and selectivity coefficients of several known ISEs have been improved by several orders of magnitude and novel, nonclassical response principles have been introduced [149, 150]. To achieve nano- and picomol/L detection limits, the ISEs were often used under nonequilibrium conditions in which engineered concentration gradients [151] or external current [152, 153] were utilized to eliminate minor ionic fluxes across the membrane which contaminated the sample solution in contact with the sensing membrane. In view of this, a recent IUPAC technical report [154], emphasized the need for updated or refined IUPAC recommendations for performance evaluation criteria for preparation and measurement of macro and microfabricated ion-selective electrodes. IUPAC called for a cautioned approach to the existing criteria while assessing the performance of any new ISE. A number of approaches have been identified that are aimed at improving the detection limits and also the selectivity coefficients and need a broad consensus for a final recommendation by IUPAC. For example, to improve the selectivity coefficients out of three approaches identified, IUPAC observed that two are somewhat cumbersome and thus not practical while the third one requires use of strong chelating agents [155, 156] or ion-exchangers [157] in the inner filler solution (IFS), which set a very low primary ion concentration in the IFS and preclude the primary ion leaching toward the sample. While these approaches apparently give improved detection limits and selectivity coefficients, identification and procurement of suitable ion exchangers or chelating reagents is not always feasible. In fact attempts to procure commercially the ion exchange resin used in literature for determining unbiased selectivity coefficients [158, 159] for its use in our ISE could not materialize. In view of these constraints and as the ISE fabricated in the present investigations used a new ionophore for the first time, it was felt that MMP method could be employed without sacrificing other parameters to assess the performance of the ISE.

Many of the Cs-selective ISEs available or reported in literature have limited lifetime of maximum of a couple of months only. One of the aims of present investigation is to fabricate an ISE for Cs with a reasonably long life. In the present part, the performance of cesium ion selective PVC based membrane electrode employing 5-(4′-nitrophenylazo)25,27-bis(2-propyloxy)26,28-dihydroxycalix[4]arene as an ionophore was studied. Studies were carried out to optimise the membrane composition to obtain the best performance for cesium by varying plasticizers, ion additives and concentration of inner filling solution.

5.1.2. Experimental

5.1.2.1. Instrument

Orion model 720A potentiometer was used to measure the potentials and pH. Orion double junction Ag/AgCl (model 9002) was used as a reference electrode. A pH electrode (Eutech instruments, Singapore) was used to measure the pH of the solution.

5.1.2.2. Materials

The ionophores 5-(4′-nitrophenylazo)25,27-bis(2-propyloxy)26,28-dihydroxycalix[4]arene was synthesized by Prof. H.M. Chawla, Indian Institute of Technology, Delhi, India and his group. The material is used as received from Prof. Chawla group without any further purification. The structure of the compound is given in figure 5.1.

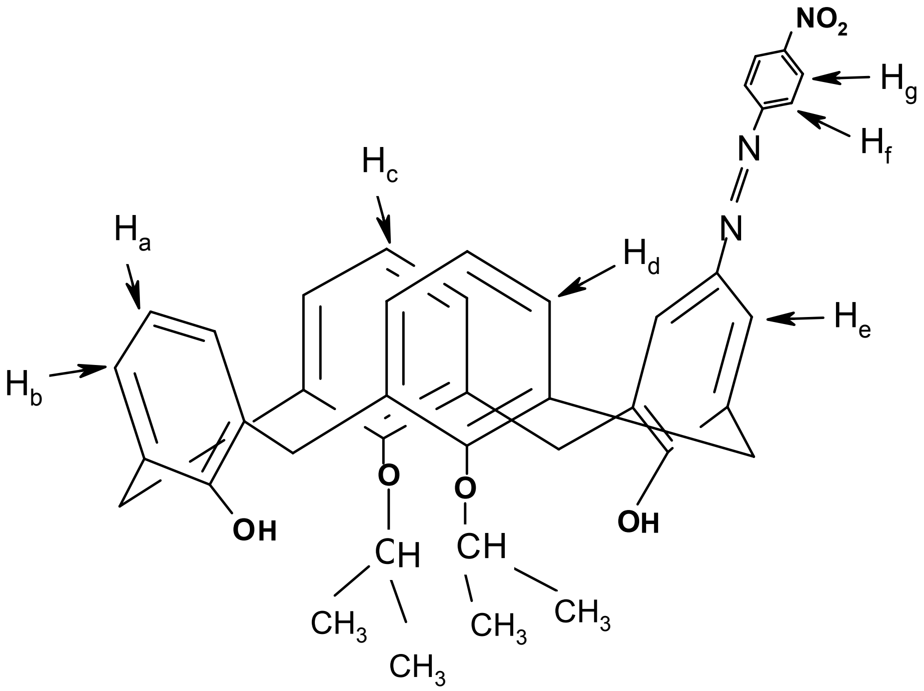


Fig. 5.1. Structure of ionophores.

The other membrane components, 2- nitro phenyl octyl ether (oNPOE), Tris (2-ethyl hexyl) phosphate (TEHP), Nitro phenyl pentyl ether (NPPE), potassium tetrakis (perchloro phenyl) borate (KTpClPB), high molecular weight poly vinyl chloride (PVC) were of Fluka, Switzerland make. BDH, UK make Bis (2-ethyl hexyl) sebacate (DOS), Merk, India make Sodium tetra phenyl borate (NaTPB), and G-Merk, Germany make Tetra hydrofuran (THF) were used. The salts of analytical reagent grade, CsCl, RbCl, KCl, NaCl, $SrCl_2$, $BaCl_2$, $MgCl_2$, $CaCl_2$, NH_4NO_3, $Pb(NO_3)_2$, $Ce(NO_3)_3$, $CuSO_4$, $ZnSO_4$, $NiSO_4$, HCl, NaOH were used wherever necessary. For preparing standard CsCl solution, CsCl salt was heated at 383 K for 2 hrs and kept in desiccator. This salt was used for preparing standard CsCl solution. High purity de-ionised water obtained from milli Q academic apparatus (Billerica, MA, USA) was used to prepare all solutions and dilutions.

5.1.2.3. Membrane preparation

The composition of PVC matrix membrane (M) was ~1.0 wt% ionophore, ~33 wt% PVC and ~65.5 wt% plasticizer. Additionally ~ 0.5 wt% ion additive ((KTpClPB) was also used. The components were dissolved in freshly distilled 6.0 ml of tetrahydrofuran by stirring for 10 minutes with magnetic stirrer. The solution was homogenized in ultra sonic for 10 minutes and then poured into a 5.0 cm inner dia Petri dish. By gradual evaporation of solvent, THF, for 48 hours at room temperature, a transparent membrane was obtained. By keeping the same composition of the membrane as mentioned above, four membranes were prepared with different plasticizers, namely, oNPOE (M1), DOS (M2), NPPE (M3), and TEHP (M4). Similarly to study the effect of ion additive, one more membrane was also prepared with same composition by taking oNPOE as plasticizer and NaTPB as ion additive (M5). To study the role of ionophore in ISE, membrane M6 was prepared without ionophore and taking all other membrane components, oNPOE as plastcizer and KTpClPB as ion additive.

5.1.2.4. Electrode fabrication and conditioning

The resulting membrane was gently peeled off from the Petri dish and a disc of 7 mm diameter was cut out using a punch borer. This membrane was attached to Fluka ion selective electrode body (cat. No. 45137). ISE was filled with 0.1 M CsCl as inner filling solution and conditioned for 48 hours by immersing in 0.1 M CsCl.

5.1.2.5. EMF measurement

All measurements were carried out at room temperature (295 ± 1 K) employing ORION-720A model digital potentiometer. The potential was measured under constant stirring of the test solution with respect to double junction Orion Ag/AgCl reference electrode (cat. No.9002), with Orion inner filling solution (cat. No. 900002) and 10% KNO_3 as outer filling solution.

The cell configuration is

Ag/AgCl / Inner filling solution(0.1M CsCl) // Membrane // Test solution // 10% KNO_3 // Orion inner filling solution (900002)/Ag/AgCl

5.1.2.6. Measurements at different pH

To study the effect of pH on response of ISE for Cs(I), the EMF was measured with ISE having membrane M1 and 10^{-1} M CsCl as inner solution. 10^{-1} M CsCl aliquots (3.0 mL) were taken and 20 mL of de-ionised water was added. In each case pH of these solution was adjusted in the range 2 to 12, by adding dilute HCl and NaOH.

5.1.2.7. Determination of Cs in simulated nuclear waste solution

For these experiments, the data of the compositions of Indian pressurized heavy water reactor (PHWR) fuel reprocessing waste, operated for 6700 MWD/ton was prepared by the Waste Immobilization Plant (WIP), BARC, Mumbai, India. Two types of high level simulated active waste solutions designated as SIM 1 and SIM 2 were used for these experiments. Between these, only SIM 1 contained U(VI), while the compositions (table 5.3.) of the other metal ions were same. 5.0 mL of the simulated waste was taken in a 50 mL glass beaker. The solution was evaporated to dryness over a hot plate. After cooling down to room temperature, 5.0 mL de-ionized water was added and again heated to dryness. The salts left were dissolved and diluted to 30 mL with de-ionised water. The pH was in the range 3 to 4. The potential was measured employing ISE with membrane M1, 10^{-1} M CsCl as inner filling solution. For evaluating the loss of cesium during the evaporation cycles, standard cesium solutions were analysed employing the same methodology used for simulated waste solutions.

5.1.2.8. Lifetime of ISE

To ascertain the lifetime of the ISE, slope of calibration plot for Cs was measured over the concentration range of 10^{-5} to 10^{-1}M CsCl periodically. For first two weeks, every day, from third week to fifth week every alternative day and from sixth week onwards once in a week slope of calibration plot was measured. Selectivity coefficients were determined after every three months. Whenever not in use, the Cs ISE was left immersed in 0.1 M CsCl solution.

5.1.3. Results and Discussion

It should be mentioned that recently [160], the use of highly diluted IFSs with well-controlled ion activities (e.g., buffered) is recommended [151] as concentrated IFS has been shown to be disadvantageous as it may contribute to primary ion leaching across the membrane into the analyte solution. The concentration of the IFS should be somewhat lower or should match the concentration of the most dilute analyte solution [161]. However, matching the concentration of the sample is not a realistic alternative for analysis of sample lots with high variability in analyte concentrations. Use of very dilute solutions as IFS without resorting to well-controlled ion activities may result in leaching of primary ion from the analyte solution into the membrane which leads to change phase boundary potential on IFS side. Controlled ion activities may be realised either through addition of suitable buffers, ion exchangers or chelating reagents. Due to non-availability of required ion exchanger and as a new ionophore is being used for the first time, it was decided to adopt conventional approach.

5.1.3.1. Response of ISE for Cs with different membranes

Response of ISE for cesium was measured with membranes M1, M2, M3 and M4 after conditioning with 10^{-1} CsCl. The best response was observed with ISE with membrane M1. The results are given in pictorial form in figure 5.2. Hence oNPOE is used as plasticizer for further studies. To study the effect of ion additives, membranes M1 and M5 with two different ion additives namely KTpClPB and NaTPB were prepared and response was measured. To study the response and selectivity of other membrane components to cesium (without ionophores), response of ISE with membrane M6 was measured. Response for cesium with all these membranes is also given figure 5.2. It is found that membrane M1 has given the best response i.e. 56 mV for decade change in the concentration of Cs. The ISE with membrane M6, has also given response for cesium with slope 35 mV/ decade. This may be due to ion exchange of cesium with ion additive in membrane.

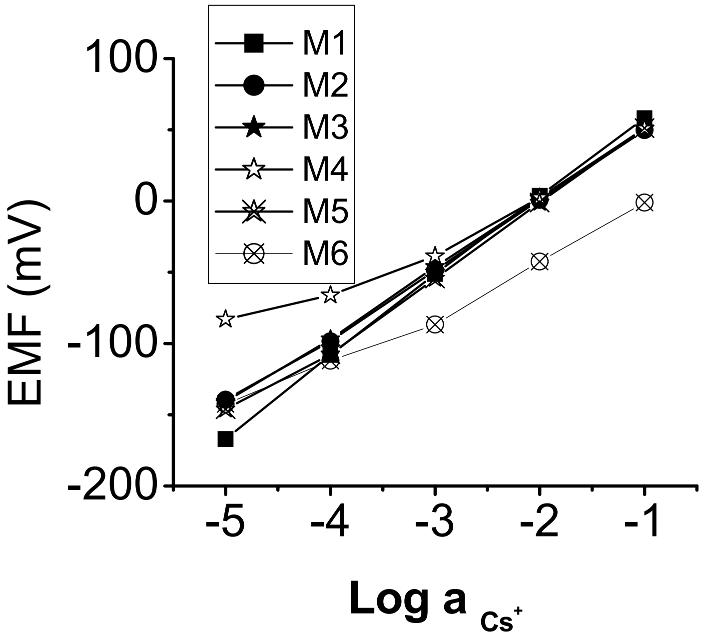


Fig. 5.2. Response of ISE for cesium with different membranes.

5.1.3.2. Selectivity Coefficients

The selectivity is one of the important characteristics of ion selective electrode. It often determines whether a reliable measurement in the target sample is possible [139]. Several methods are available to determine selectivity coefficients like fixed interference method, separate solution method and matched potential method (MPM). IUPAC recommended matched potential method to obtain more reliable data [148]. Hence the selectivity coefficients were determined employing matched potential method. Selectivity for Cs over the several ions like Rb^+, K^+, Na^+, NH_4^+, Sr^{+2}, Ba^{+2}, Ca^{+2}, Mg^{+2}, Cu^{+2}, Pb^{+2}, Zn^{+2}, Ni^{+2} and Ce^{+3} was determined with ISE employing all membranes M1 to M6. The selectivity coefficients with all membranes are given in the table 5.1. From the table, it can be seen that selectivity for Cs is superior for ISE with membrane M1. Hence, for further studies, membrane M1 was used.

Table 5.1. Selectivity coefficients for various elements.

Interfering Element (I)	Selectivity Coefficient -Log K^{MPM}Cs/I					
	M1	M2	M3	M4	M5	M6
Rb^+	0.85	0.19	0.70	0.69	0.74	0.64
K^+	2.27	0.30	2.02	1.98	2.22	1.38
Na^+	3.13	0.83	3.09	3.57	3.10	2.62
Sr^{+2}	3.51	2.67	3.37	3.63	3.66	3.55
Ba^{+2}	3.37	2.90	3.17	3.10	3.51	3.25
Ca^{+2}	3.67	3.17	3.51	3.58	3.43	3.05
Mg^{+2}	3.96	3.16	3.66	3.56	4.07	3.52
Pb^{+2}	3.20	1.50	3.00	1.20	1.68	2.68
Zn^{+2}	3.94	3.20	3.85	3.35	3.60	3.65
Ni^{+2}	4.08	3.23	3.62	3.04	3.57	3.12
Cu^{+2}	3.27	2.50	3.58	2.40	3.27	3.02
Ce^{+3}	3.57	3.25	3.02	3.02	2.85	2.95
NH_4^+	1.58	1.52	1.55	1.42	1.38	1.29

5.1.3.3. Effect of inner filling solution

Effect of inner filling solution was studied by filling 10^{-1} and 10^{-3} M CsCl as an inner filling solutions for two independent ISEs and conditioned with respective solutions for 24 hrs. The response was measured for cesium and observed that both are linear for cesium in the range of 10^{-1} to 10^{-5}. A typical response graphs are shown in figure 5.3. There is no significant difference in detection limit for cesium with both the ISEs (3.72E-06 M Cs with 10^{-3} M CsCl inner filling solution, 4.6E-06 M Cs with 10^{-1} M CsCl inner filling solution). However the response time, slope of the curve between the EMF and concentration and selectivity for cesium are better with 10^{-1} M CsCl as an inner filling solution. Hence 10^{-1} M CsCl was selected as an inner filling solution.

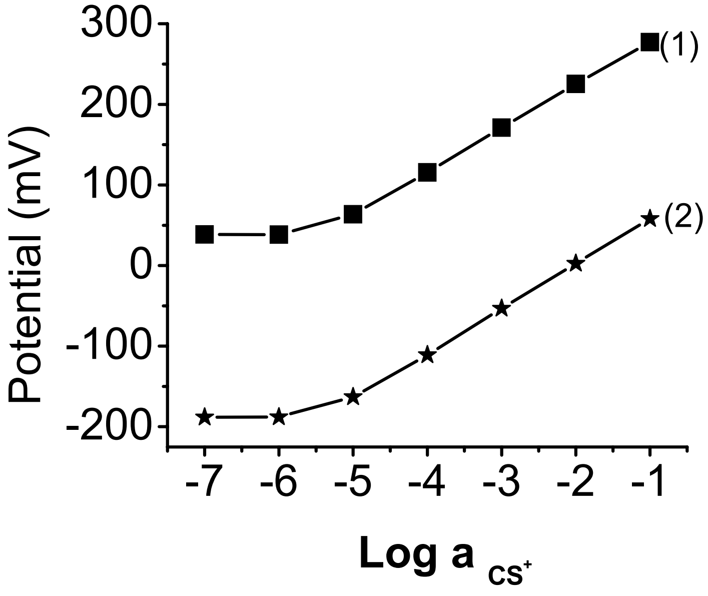


Fig. 5.3. Response of ISE for cesium employing membrane M1, with (1) 10^{-3} and (2) 10^{-1} M CsCl as an inner filling solutions.

5.1.3.4. pH Dependence

To evaluate the effect of pH on the response of ISE, 10^{-2} M CsCl solutions maintained at different pH were taken. The response was measured with ISE for cesium. Potential versus respective pH of solution was plotted. The results are shown in figure 5.4. It can be seen from the figure that the response of ISE for Cs is constant and stable over the pH range of 3 to 11. The increase in the potential at higher pH may be due to the increase in sodium ions. The discrease in potential at lower pH may be due to failure of **Donnan** membrane equibrium [132].

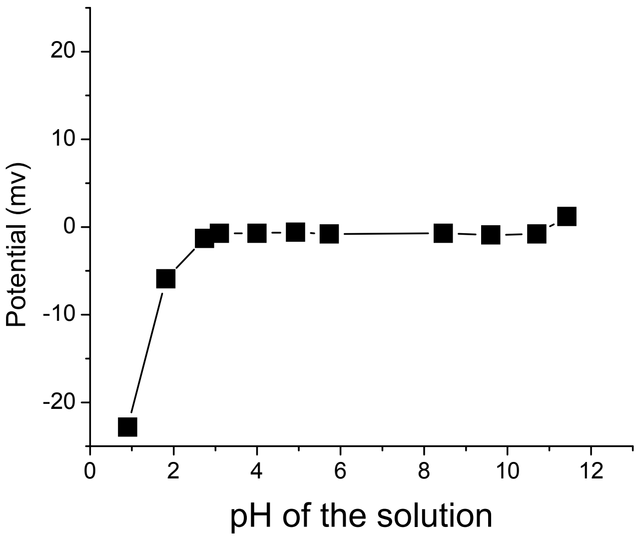


Fig. 5.4. Response of ISE for 10^{-2} M Cs^+ at different pH.

5.1.3.5. Linearity, Detection limit and Response time

The ISE with membrane M1 and 10^{-1} M CsCl as inner filling solution gave a response for cesium over the concentration range 10^{-5} – 10^{-1} M. The Nernstian slope of the response is 56 mV per decade for Cs. Detection limit of the ISE is 4.6 x10^{-6} M Cs. The response is fast and the time of response is less than the 20 seconds.

5.1.3.6. Lifetime of the ISE

Lifetime or durability of ISE is one of the important factors in deciding the applicability of ISE. One of the criteria to assess the lifetime is the extent of leaching of the ionophore from the membrane. This in turn depends on the properties of the plasticizer and the additive being used and their compatibility with ionophore. Based on this criteria it was found that for the present Cs-ISE developed, up to 37 weeks (~9 months), there was no significant change in the slope of calibration plot for cesium (56 ± 2 mV per decade concentration change in Cs), linearity (10^{-5} to 10^{-1} M CsCl) and selectivity coefficients. After that, even though slope is 56 ± 2 mV, linearity was decreased by one order (10^{-5} - 10^{-1} M Cs to 10^{-4} – 10^{-1} M Cs). After 40 weeks, slope was also decreased to 50 mV. This is a significant improvement over the existing Cs-ISE systems of similar design in terms of cost competitiveness.

5.1.3.7. Comparison with literature reports

Characteristics of developed ISE was compared with reported ISEs of Cs with various calix[4] arene componds. Details are given in table 5.2. Selectivity and applicable range for Cs is well within the range of reported literature. Lifetime of the present electrode was 9 months. This is the longest lifetime for membrane-based cesium ISE so far developed or reported.

Table 5.2. Comparison of present cesium ion selective electrode with previously reported.

Inophore	Range of applicability (M Cs)	Selectivity Coefficient - Log K^{MPM}Cs/I				Life Time	Ref. No.
		Rb	K	Na	NH_4		
Diisopropyl dihydroxy calix[4] mono azo paranitro phenyl aniline	$10^{-5} – 10^{-1}$	0.85	2.27	3.13	1.58	9 months	Present work
Biscalix[4]arene	$10^{-5} – 10^{-1}$	--	0.90	2.20	1.3	1 month	139
Bis(1-propoxy) calix[4]arene dibenzocrown-6	10^{-6}- 10^{-1}	0.80	2.16	4.88	1.90	--	137
Diisopropoxy calix[4]arene crown-6	10^{-6}- 10^{-1}	0.89	2.18	4.46	1.98	--	138
Calix[4] crown ether ester	$5.0x10^{-6}$- 10^{-1}	--	2.0	1.30	1.50	4 month	136

5.1.3.8. Application: Determination of Cs in simulated high level active waste

The composition of simulated high level active waste is given in table 5.3. Simulated waste solution will be at about 3.0 M in HNO_3. Since ISE is giving constant response over the pH range 3 to 11 and the nuclear waste solutions will be at about 3 M in HNO_3 the acidity has to be brought down to this level. Therefore, the solution was evaporated repeatedly and dissolved in de-ionised water. The resultant solution had the pH in range of 3 to 4. Concentration of cesium in these solutions was determined after calibrating the ISE with standard CsCl solution. To check the loss of cesium during evaporation, standard CsCl solution aliquots were taken and Cs concentration was determined adopting the same procedure as mentioned for simulated waste solutions. It is found that there is no loss of cesium. The method has been evaluated by analysing standard CsCl solution aliquots along with simulated waste solution aliquots by adopting same experimental procedure. The method has been authenticated by standard addition method. Standard CsCl solution aliquots were added to simulated waste solutions and employing same procedure Cs concentration was determined. Results are agreed within ± 10% in both cases, i.e. with and without standard addition. Since selectivity coefficients were not determined for several elements present in simulated waste, the present method has been validated with an independent method, Atomic Absorption Spectroscopy (AAS). Results are given in table 5.4. Results agreed well in both the methods. Hence it may be concluded that there is no interference from elements like Fe, Cr, Mn, U etc.

Table 5.3. Composition of the simulated high level active waste.

Element	Concentration (g/L)	Element	Concentration (g/L)
Fe	0.72	La	0.18
Cr	0.12	Pr	0.09
Ni	0.11	Nd	0.12
Na	5.5	Sm	0.086
K	0.22	Cs	0.24
Mn	0.43	Y	0.06
U	6.34	Zr	0.004
Sr	0.03	Mo	0.14
Ba	0.06	Ce	0.06

Table 5.4. Validation of the method.

Sample ID	Present Method (ISE) (mg/L)*	AAS (mg/L)*
SIM-01	202 ± 10	212 ± 10
SIM-02	228 ± 11	228 ± 10

* Mean of five determinations with standard deviation.

5.1.4. Conclusion

Ion selective electrode for cesium was fabricated with 5-(4′-nitrophenylazo)25,27-bis(2-propyloxy)26,28-dihydroxycalix[4]arene as ionophore showing good selectivity for Cs over other alkali, alkaline, transition and actinide elements. Developed ISE could be operated over wide range of pH from 3 to 11. Life time of the electrode is 9 months which is the highest life for any membrane based Cs - ISE so far developed.

Part II: Cesium ion selective electrode based on calix[4]arene crown-6 compounds

5.2.1. Introduction

The development of Cs- ISE with 5-(4′-nitrophenylazo)25,27-bis(2-propyloxy)26,28-dihydroxycalix[4]arene gave selectivity coefficient for Cs with respect to Na, (Log $K_{Cs, Na}$) -3.13. One of the purposes of Cs-ISE has been to determine Cs in nuclear waste streams where Na concentration is very high compared to Cs concentration. Hence selectivity ($K_{Cs, Na}$) has to be improved for achieving more confidence on Cs results.

Sachleben et. Al [162] studied solvent extraction of cesium and its selectivity over other alkali ions with various dialkyloxy calix[4] arene crown-6 compounds. Also Simon et al [163] studied solvent extraction of cesium from acidic high level active waste solution employing various 1,3 alternative dialkyloxy calix[4] arene crown-6 extractants and achieved good separation efficiency and selectivity for cesium over other alkali metal ions especially sodium ion ($K_{Cs, Na}$) ~34000). Hence studies have been carried out to develop ion selective electrode for cesium employing 25, 27-dihydroxycalix[4]arene-crown-6 (L1), 5,11,17,23-tetra-tert-butyl-25,27-dimethoxycalix[4]arene-crown-6 (L2) and 25, 27-bis(1-octyloxy)calix[4]arene-crown-6 (L3) as an ionophores.

The measuring range of conventional membrane based ion selective electrodes (ISEs) lies between 1 and 10^{-6} M. Extensive research to realize low detection limit of ISEs has shown that the detection limit is not an inherent property of ISEs but is determined by a small flux of primary ions from the organic sensing membrane into its aqueous surface layer. The composition of inner filling solution, if not selected carefully has been shown to be the most important source of these fluxes due to the enhancement of co-extraction or ion exchange processes at the inner solution/ membrane interface. In addition to biasing the lower detection limit, trans-membrane ion fluxes also bias the ionophore based selectivity of the sensor by affecting the measurement of potential even if measurements are taken in pure solutions of strongly discriminated ions [157]. It was found that selectivity coefficients thus determined represent upper limits rather than true (thermodynamic) values, which may be better by many orders of magnitude than those determined by conventional methods.

Due to the reasons already enunciated in Part I, to improve the selectivity and detection limit for Cs, cation exchange resin Dowex-50W is used to maintain low and constant activity of Cs^+ in inner filling solution.

5.2.2. Experimental

5.2.2.1. Ionophores, Membrane components and chemicals

All three ionophores 25, 27-dihydroxycalix[4]arene-crown-6 (L1), 5,11,17,23-tetra-tert-butyl-25,27-dimethoxycalix[4]arene-crown-6 (L2) and 25, 27-bis(1-octyloxy)calix[4]arene-crown-6 (L3) were synthesized employing procedure as mentioned in literature [75] by Dr. S. Chattopadhyay and his group, Bio-organic Division, BARC. The other membrane components were procured as mentioned in part I.

5.2.2.2. Membrane Preparation

Keeping the same membrane composition as mentioned in part I, various membranes were made with different ionophores, plasticizers and different amounts of ion additive. Details are given table 5.5

5.2.2.3. Inner filling solution preparation

About 5 g of the cation exchange resin Dowex - 50W (H^+ form) was taken in a glass beaker and was equilibrated with 1 M NaOH (50 mL) for about 14 hours under constant stirring. The resulting Na^+ form of resin was washed with deionised water several times and air dried for about 48 hours. The air dried resin was wrapped in tissue paper and kept in a desiccator for 24 hours to remove traces of moisture. With a view to optimizing the amount of resin required and also determining equilibrium concentration of Cs, it was necessary to determine the selectivity of this resin for cesium over sodium [157], ($K_{Cs,Na} = m_{cs,\ resin}.m_{Na,aq} / m_{Na,\ resin}.m_{cs,\ aq}$, where m is content of ion in moles). 0.2160 g of dry resin in Na^+ was taken and 5 ml of 6.0×10^{-3} M CsCl was added and stirred for about 12 h. Concentration of Cs in equilibrated solution was determined with ISE 9 and was found to be 1.32×10^{-4} M. This gives $K_{Cs,\ Na} = 148$. The cation exchange capacity of the resin was quoted as 5.6 meq/g and this value is taken for calculations. The inner filling solution was prepared by equilibrating 1.0730 g of dry Na^+ form resin with 25 mL of 6.0×10^{-4} M CsCl solution for 12 h. Cesium concentration in equilibrated solution was found to be less than 10^{-7}M Cs^+. After filling this solution along with resin as an inner filling solution, ISE was conditioned with 10^{-7} M CsCl for 24 h.

5.2.2.3. EMF measurement

All measurements were carried out at room temperature (295 ± 1 K) employing ORION-720A model digital potentiometer. The potential was measured under constant stirring of the test solution with respect to double junction Orion Ag/AgCl reference electrode (cat. No.9002), with Orion inner filling solution (cat. No. 900002) and 0.1 M lithium acetate (LiOAc) as outer filling solution.

The cell configuration is

Ag/AgCl / Inner filling solution(~ 10^{-8} M CsCl with resin) // Membrane // Test solution // 0.1 M LioAc // Orion inner filling solution (900002)/Ag/AgCl

The activities of cesium (I) were calculated according to the Debye–Huckel procedure, using the following equation [164]

$$Log\gamma = -0.511z^2\left[\frac{\mu^{\frac{1}{2}}}{1+1.5\mu^{\frac{1}{2}}} - 0.2\mu\right] \ldots\ldots (1)$$

Where γ is activity coefficient, μ is ionic strength the solution and z is the valency of the ion.

5.2.2.4. Measurements at different pHs

To study the effect of pH on response of ISE for Cs(I), the EMF was measured with ISE 7. Aliquots (3.0 ml) of CsCl solution (10^{-1} M) were taken and diluted with de-ionized water (20 ml). The pHof each solution was adjusted in the range 2 to 12 by adding appropriate amounts of dilute aqueous HCl and NaOH solutions and made final concentration of Cs(I) as 10^{-2} M.Similar solutions of CsCl (10^{-4} M)werealso made at different pHand the response was measured.

5.2.2.5. Determination of Cs(I) concentration in simulated nuclear waste solutions

As mentioned in part I of this chapter, these solutions are highly acidic (~3 M HNO_3 media),their pHs were brought down between 4 to 11 prior to the measurements. For the calibration purpose, high level simulated waste solutions were also prepared with the same composition and acidity without adding the Cs-salt. The Cs(I) content in the original simulated waste solutions was determined with ISE 7 employing three different procedures.

i. ***Procedure 1:*** Eight well-cleaned 100 ml glass beakers were numbered sequentially. Aliquots (5 ml) of two sets of simulated waste solution were taken in duplicate in the beakers (nos. 1-4). Similarly, the waste solutions without Cs-salt (5 ml), prepared for calibration, were taken in another set of beakers (nos. 5-8). Aqueous CsCl solution (3 ml, 10^{-2} M) was added to the beakers 5 and 6, while CsCl solution (3 ml, 10^{-3} M) was added to the beakers 7 and 8.The solutions in all beakers were evaporated to dryness over a hot plate. After cooling to room temperature, de-ionized water (5.0 ml) was added to each of the beakers, followed by heating to dryness again. The procedure was repeated two times. Finally, de-ionized waterwas added to the salts left over in beakersand diluted to 30 ml. The pH was measured and found to be in the range of 4 to 5. The potential was measured employing ISE 7.

ii. ***Procedure 2:*** Aliquots of simulated waste solutions without and with standard CsCl solutions were taken in eight beakers as mentioned in procedure 1. De-ionized water (12 ml) and two drops of phenolphthalein solution were added to all the beakers. After neutralizing the solutions with 3M LiOHsolution, thefinal volume was made up to 30 ml, and the potential was measured employing ISE 7.

iii. ***Procedure 3:*** The Cs(I) concentration was determined by standard addition and subsequent dilution method. In this, 5.0 ml aliquots from the two test simulated waste solutions in quadruplicateswere taken in eight beakers. Aqueous CsCl solution (3.0 ml, 10^{-2} M) was added to the beakers 3, 4, 7 and 8. All thesolutions were neutralized with 3 M LiOH and diluted toa final volume of 30 ml. The potential in all thesolutions was measured employing ISE 7. The solutions in beakers 3, 4, 7 and 8 were further diluted with de-ionized water up to 60 ml, and the responses were measured employing ISE 7.

5.2.2.6. Lifetime of ISE

To ascertain the lifetime of ISE 7, slope of calibration plot for Cs(I) over the concentration range of 10^{-7} to 10^{-2}M and the selectivity coefficients for all the alkali metal ions and ammonium ion were measured periodically employing ISE 7. The measurement schedule was as follows: (i) every day for the first two weeks; (ii) every alternate day during the third to fifth weeks; (iii) once a week during the sixth to fifteenth weeks; and (iv) every 15 days sixteenth week onwards tillforty six weeks. The ISE 7 was left immersed in 10^{-7} M CsCl solution, when not in use.

5.2.3. Results and Discussion

5.2.3.1. Responses of different ISEs for Cs ions

For these studies, six newly designed ISEs (designated as ISE 1 to ISE 6) were fabricated using the ionophores L1 to L3, oNPOE or DOS as the plasticizer and KTpClPB (50 mol%) as the ion additive. Measurement of the responses of the ISEs for Cs(I) ions in the concentration range of 10^{-2} to 10^{-9} M revealed best result with ISE 5, made of L3,oNPOE and KTpClPB. For further optimization of the performance of the ISE, the composition of ISE 5 was varied by changing the KTpClPB content to 40 and 30 mol% to obtain two additional ISEs, designated as ISE7 and ISE8 respectively. The response characteristics of all the ISEs and their respective compositions are given in table 5.5. Their results showed superior performance by ISE 7, amongst the chosen ISEs. Subsequently, to see the role of the resin in IFS, another ISE (ISE 9) was prepared maintaining the same composition as that of ISE 7, but changing the IFS with 10^{-3} M CsCl (without resin), and its response for Cs ions was also measured (table 1). The results showed that the DLs and response of ISEs were improved by using low and constant activity of Cs ions along with resin as an inner filling solution.

5.2.3.2. Selectivity Coefficients

The selectivity is one of the important characteristics of ion selective electrode. It often determines whether a reliable measurement in the target sample is possible. Several methods like fixed interference method, separate solution method and matched potential method (MPM)are available to determine selectivity coefficients. IUPAC recommended separate solution method when low activity of primary ion and high activity of interfering ion is used as inner filling solution with the help of ion exchange resin [154]. Hence the selectivity coefficients were determined employing separate solution method. Selectivity for Cs over several ions like Rb^+, K^+, Na^+, Li^+, NH_4^+, Sr^{+2}, Ba^{+2}, Ca^{+2}, Mg^{+2}, Cu^{+2}, , Zn^{+2}, Ni^{+2}, $Pb^{+2}$and Hg^{+2} was determined employing all ISEs (1 to 9). The selectivity coefficients data are given in the table 5.6. From the table, it can be seen that selectivity for Cs is superior for ISE 7. Hence, further studies are carried out with this ISE 7. One advantage of the developed ISE is very large selectivity of Cs over sodium ($\log K_{Cs/Na} = -4.68$). Hence it would be very useful to determine Cs in nuclear waste solution where low concentration of Cs has to be determined in presence of high concentration of Na. In addition, ISE 7 also showed a low DL value (8.48×10^{-8} M) for the Cs ions. Hence, further studieswere carried out with ISE 7 only.

Table 5.5. Comparison of response of ISE with different ionophores, plasticisers and amount of ion additive.

ISE No.	ISE 1	ISE 2	ISE 3	ISE 4	ISE 5	ISE 6	ISE 7	ISE 8	ISE 9*
Ionophore	L1	L1	L2	L2	L3	L3	L3	L3	L3
Plasticiser	NPOE	DOS	NPOE	DOS	NPOE	DOS	NPOE	NPOE	NPOE
Ion Additive mol%	50	50	50	50	50	50	40	30	40
Linear Range	10^{-5}-10^{-2}	10^{-5}-10^{-2}	$5x10^{-6}$-10^{-2}	10^{-5}-10^{-2}	$5x10^{-7}$-10^{-2}	10^{-6}-10^{-2}	10^{-7}- 10^{-2}	$5x10^{-7}$-10^{-2}	10^{-5} -10^{-2}
Nernestian slope (mV/decade of Cs)	55.8	50.3	53.3	53.7	57.0	55.6	56.3	57.3	55.8
DL	3.72E-6	4.46E-6	3.16E-6	3.54E-6	2.82 E-7	8.62 E-7	8.48 E-8	3.9E-7	5.45E-6

*Inner filing of this ISE is 10^{-3} M CsCl

5.2.3.3. pH Dependence

To evaluate the effect of pH on the response of ISE, the response of ISE 7 was measured in 10^{-2} M and 10^{-4} M CsCl solutions maintained at different pH. Potential versus respective pH of solution was plotted. The results are shown in figure 5.5. It can be seen from the figure that the response of ISE for Cs is constant and stable at pH of the solution is more than 4 for both the concentrations. The decrease in potential at lower pH may be due to failure of **Donnan** membrane equilibrium [132].

5.2.3.4. Linearity and response time

ISE 7 showed a Nernstian response for Cs ions over the concentration range 10^{-7} – 10^{-2} M, with a slope of 56.6 mV per decade for Cs ions (figure 5.6). The response was fast with the response time less than 10 seconds.

Table 5.6. Selectivity coefficients of various ions determined by separate solution method.

Interfering Element (I)	Selectivity Coefficients (-Log $K_{Cs^+, I}$)								
	ISE 1	ISE 2	ISE 3	ISE 4	ISE 5	ISE 6	ISE 7	ISE 8	ISE 9
Rb^+	0.02	0.04	0.68	0.60	1.06	1.02	1.22	0.98	0.89
K^+	0.00	0.19	1.32	1.92	2.30	2.16	2.37	2.05	2.27
Na^+	1.89	1.79	2.30	2.47	4.52	4.32	4.68	4.60	4.35
Li^+	3.39	3.43	3.07	2.94	5.56	5.22	5.20	5.10	5.47
NH_4^+	0.68	0.59	1.31	2.06	2.17	1.98	2.14	1.85	2.02
Sr^{+2}	4.34	4.64	3.28	5.35	6.33	6.36	5.93	5.85	5.40
Ba^{+2}	4.35	4.13	2.38	5.66	6.57	6.38	6.12	6.10	6.26
Ca^{+2}	4.69	4.74	3.83	5.61	6.09	5.81	6.13	5.95	5.97
Mg^{+2}	4.37	4.57	4.14	5.52	5.92	5.63	6.02	5.78	5.58
Zn^{+2}	4.28	4.58	4.30	5.51	5.74	5.46	5.86	5.58	5.46
Cu^{+2}	4.10	4.37	3.55	5.05	5.62	5.33	5.58	5.03	6.02
Ni^{+2}	4.15	4.39	3.44	5.21	5.58	5.40	5.48	5.36	5.46
Pb^{+2}	3.21	3.59	3.33	2.11	4.68	4.31	4.58	4.28	3.86
Hg^{+2}	4.03	3.56	3.50	357	4.75	4.35	4.85	4.32	4.21

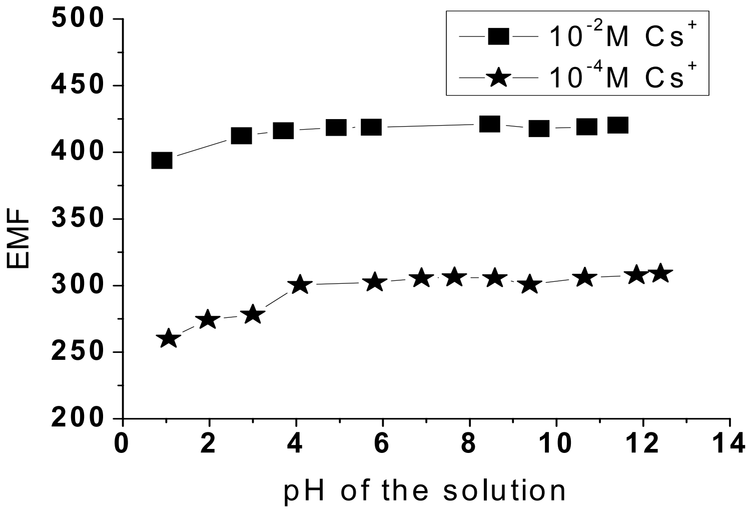


Fig. 5.5. Response of ISE for 10^{-2} and 10^{-4} M Cs^+ at different pH the solution.

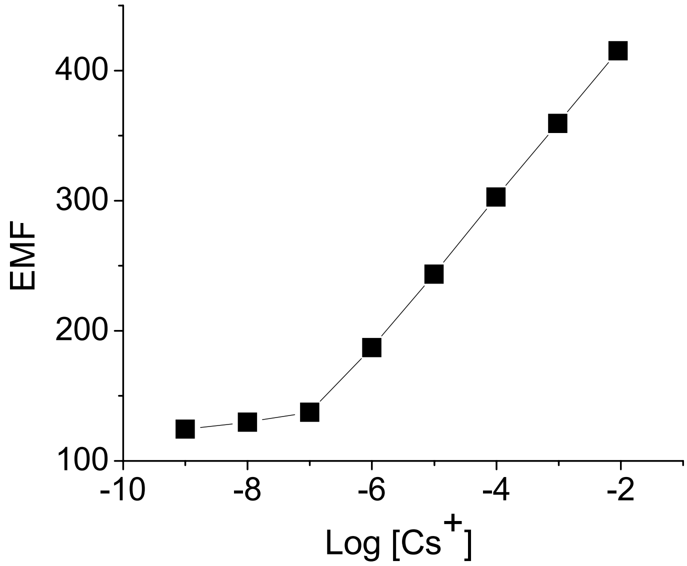


Fig. 5.6. Response of ISE for cesium (ISE 7, Table 5.5).

5.2.3.5. Life time of the ISE

It was found that for the present Cs-ISE, up to 42 weeks (~10 months), there was no significant change in the slope of calibration plot for cesium (56 ± 2 mV per decade concentration change in Cs), linearity (10^{-7} to 10^{-2} M CsCl) and selectivity coefficients. After 44 weeks, the slope was decreased to 54 mV and then after 15 days slope was further decreased to 48 mV. Hence it was concluded that life time of ISE is 10 months. This is a significant improvement over the existing Cs-ISE systems of similar design in terms of cost competitiveness.

5.2.3.6. Comparison

Characteristic features of the developed ISE were compared with reported ISEs of Cs with various ionophores. Details are given in table 5.7. Selectivity and applicable range of the ISE for Cs is well within the range of reported literature. The lifetime of the present electrode is 10 months. This is the longest lifetime for membrane-based cesium ISE so far developed or reported.

5.2.3.7. Application- Determination of Cs in simulated high level active waste

The ISE 7 was calibrated using the solutions in the beakers 5 to 8 and employing the procedures 1 and 2 given in the Experimental section. The procedures 1 and 2 gave the

Table 5.7. Comparison of present cesium ion selective electrode with previously reported membrane based ISE of Cs.

Inophore	Detection limit (M Cs)	Range (M Cs)	Selectivity Coefficient - Log K^{MPM}Cs/I				Life Time	Ref .No.
			Rb	K	Na	NH$_4$		
2,3 Benzoquino-crown-5	$2.5x10^{-5}$	$10^{-4} – 10^{-1}$	0.47	0.99	2.38	1.40	1 month	134
Calix[4]crown ether ester	$5.0x10^{-6}$	$5.0x10^{-6} – 10^{-1}$	--	2.0	1.30	1.50	4 months	135
Bis(1-propoxy) calix[4]arene dibenzocrown-6	--	10^{-6}- 10^{-1}	0.80	2.16	4.88	1.90	--	136
Diisopropoxy calix[4]arene crown-6	$5x10^{-7}$	10^{-6}- 10^{-1}	0.89	2.18	4.46	1.98	--	137
Biscalix[4]arene	--	$10^{-5} – 10^{-1}$	--	0.90	2.20	1.3	1 month	138
Di isopropyl dihydroxy calix[4] mono azo paranitro phenyl aniline	$4.6x10^{-6}$	$10^{-5} – 10^{-1}$	0.85	2.27	3.13	1.58	9 months	140
Thiacalix[4]biscrown-6,6	$3.8x10^{-7}$	10^{-6}-$3.2x10^{-2}$	1.4	3.7	4.3	2.5	--	141
Thiacalix[4]crown-6	--	10^{-7}- 10^{-1}	2.20	3.50	5.10	3.10	--	142
Calix[4]arene tetraester	$4.9x10^{-7}$	10^{-06}- 10^{-01}	1.88	2.23	3.25	3.01	--	143
Calix[4]arenehexaethylester	--	$5x10^{-5}$-10^{-1}	1.52	2.53	3.73	2.75	1 month	144
5-(4′-nitrophenylazo)25,27-bis(2-propyloxy)26,28-dihydroxycalix[4]arene	$6.3x10^{-6}$	$2.5x10^{-5}$- 10^{-1}	0.70	1.22	2.72	1.59	18 days	147
25,27-bis(1-octyloxy)calix[4]arene-crown-6 (**L3**)	$8.48x10^{-8}$	10^{-7}-10^{-2}	1.22	2.37	4.68	2.14	10 months	Present work

calibration slope as 53.6 ± 0.4 mV/decadeand 54.2 ± 0.3 mV/decade concentration respectively. The response of the ISE to Cs ions was then measured using the solutions in beakers 1 to 4. Using procedure 3, the ISE 7 was calibrated from the potential response in beakers 3,4, 7 and 8 before and after dilution. The calibration slope was found to be 52.6 ± 0.5 mV/decade concentration. From the calibration data and potential responses in beakers 1,2, 5 and 6, the Cs(I) concentration was determined in the simulated waste solutions SIM 1 and SIM 2. In all the three procedures, only the Cs ions concentration was considered for calibration. Due to the high ionic strength of the solutions (presence of large amount of salts), activity of Cs(I) got reduced, and hence the slope of calibration deviated more from the Nernstian response. Results for all the three procedures are given in table 5.8. Since selectivity coefficients were not determined for several elements present in the simulated wastes, the present method was validated with AAS. Our ISE results agreed well with the AAS values (table 5). Hence it may be concluded that there is no interference from elements like Fe, Cr, Mn, U etc.

Table 5.8. Determination of cesium in simulated high level active waste solution and comparison with AAS values.

Sample ID	ISE (mg/L)			AAS (mg/L)[&]
	Method 1[*]	Method 2[*]	Method 3[*]	
SIM-01	205	210	212	212 ± 10
SIM-02	223	212	232	228 ± 11

[*] Mean of two determinations

[&] Mean of five determinations with standard deviation

5.2.4. Conclusion

Ion selective electrode for cesium developed with 25, 27 dioctyloxy calix[4]arene-crown-6 as ionophore has superior selectivity for Cs over other alkali, alkaline, transition elements. The ISE could be operated at pH above 4 and has been successfully employed to determine cesium content in high level simulated waste. Life time of the electrode is 10 months which is the highest life for any membrane based Cs - ISE so far developed.

Summary and important highlights of the thesis

Determination of trace elements is important and required for many applications. In nuclear technology, for example, the chemical characterisation of different materials (nuclear fuels, reactor materials, nuclear waste streams etc.) with respect to trace elements is a necessary quality assurance step. Critical trace constituents like boron which has high thermal neutron absorption cross section, need to be determined with the highest possible precision and accuracy for a rigorous quality assurance. Even though there are analytical techniques available for this purpose, but there is enough scope for further improvement in the existing methodology either in terms of extending their applicability or eliminating known limitations. In addition, many of the sophisticated instrumental analytical techniques require matrix matched reference materials for validation and quantification of analytical results. Many times these matrix-matched reference materials are not either available or accessible. The only recourse is to validate the analytical results by as many techniques based on independent theoretical principles as possible.

Statistical treatment of analytical results for evaluating the total measurement uncertainty in the final result is very crucial in trace analysis for reliable interpretation of the results. It is essential to adopt standard statistical procedures available in literature rather than simply calculate the mean and standard deviation.

The scope of the present thesis has been to develop and standardise suitable analytical methodology for determination of trace elements particularly boron and cesium, both being important from their relevance in nuclear technology. The former is important in the front-end of nuclear fuel cycle while the latter is of relevance in the back-end of the nuclear fuel cycle. In view of the requirement of boron determination in a wide variety of matrices, the investigations were undertaken to adapt as many suitable techniques as possible for different matrices. At the same time the possibility of employing more than one technique for validation of analytical results was also emphasised. Final acceptance of any analytical result is decided by the statistical treatment to which the data is subjected to. ISO recommended total measurement uncertainty principle has been adopted.

The highlights of the present investigations are

(1). Using low neutron fluxes, about 10^6 n/cm^2/Sec, boron in ppm levels was determined employing Chemical PGNAA. This is the first time chemical PGNAA has been employed to determine boron.

(2). The well known spectrophotometric method for the determination of boron in uranium compounds with curcumin after extraction with 2-ethyl hexane 1,3 diol has been modified such that the sample size is reduced from 2.5g to 0.200g. Extensive investigations have been carried out to study the reasons for nitric acid interference in methodology and to circumvent the same. These studies are essential in nuclear technology since different acids are employed to dissolve uranium compounds.

(3). To our best of knowledge, first time spectrophotometric method has been developed and employed for the determination of boron in uranium-aluminum-silicon inter metallic compound. This method has been extended to determine boron in various silicon related materials of interest in nuclear technology like SILUMIN, Al-Si alloy and U_3Si_2.

(4). Spectrophotometric method employing curcumin has been modified for the determination of boron in highly refractory material Zr-Nb alloy. Dissolution procedure has been modified suitably to prevent the loss of boron. Due to selective separation of boron with 2-ethyl hexane 1,3 diol, reported interference from tin was avoided and also precision and accuracy has been improved considerably compared with literature reports.

(5). To increase the confidence on measurand values, uncertainty in spectrophotometric method for the determination of boron was estimated by following ISO guidelines.

(6). A simple and sensitive method for the determination of boron in Zr- Nb alloy samples based on commercially available BF_4^- ISE has been developed. Conditions are optimized to determine boron with BF_4^- ISE in zirconium matrix which is forming highly stable complex with fluoride ion. This is the first time to determine boron in Zr-Nb alloy samples employing BF_4^-. To increase the confidence on measured values combined and then expanded uncertainty the methodology was estimated.

(7). The ISO recommended principle (Guide to Uncertainty measurement GUM) has been applied to the analytical results to compute the total measurement uncertainty in the analytical results. The “bottom-up” approach has been adopted for this purpose. The rationale behind using the error propagation principle to assess the individual uncertainty components particularly in calibration procedures has been elucidated clearly. This is required as many analytical techniques are based on calibration methodology for quantification of results and the GUM does not have such a provision.

(8). New ion selective electrode for cesium was developed employing 5-(4′-nitrophenylazo) 25, 27-bis(2-propyloxy)26,28-dihydroxycalix[4]arene as an ionophore . Developed ISE is having good selectivity for Cs over Na which is essential for determination of Cs in nuclear waste solutions. One of the advantages of the developed ISE is having life of nine months.

(9). Various calix[4]arene crown -6 compounds are tested for preparation of Cs ISE and best response was observed with dioctyloxycalix[4]arene crown 6 . Employing ion exchange resins in inner filling solutions, response and selectivity for cesium are improved. Employing developed ISE, Cs concentration in simulated high level nuclear waste solutions was determined employing standard addition and dilution method. The loading capacity of polymeric beads for Cs was also determined. The life time of the electrode is 10 months which is longest life time so far reported for any Cs ISE.

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List of publications forming a part of the thesis

Refereed Journals

1. Determination of boron in water samples by chemical prompt gamma neutron activation analysis,

   P.S. Ramanjaneyulu, Y.S. Sayi, T. Newton Nathaniel, A.V.R. Reddy and K.L. Ramakumar,

   Journal Of Radioanalytical and Nuclear Chemistry, 273 (2007) 411-414.
2. Determination of boron in uranium compounds by spectrophotometry and studies on effect of HNO_3,

   P.S. Ramanjaneyulu, Y.S. Sayi, V.A. Raman and K.L. Ramakumar,

   Journal Of Radioanalytical and Nuclear Chemistry, 274 (2007) 109-114.
3. Determination of boron in uranium–aluminum-silicon alloy by spectrophotometry and estimation of expanded uncertainty in measurement,

   P.S. Ramanjaneyulu, Y.S. Sayi, K.L. Ramakumar,

   Journal of Nuclear Materials, 378 (2008) 139-143.
4. Ion selective electrode for Cesium based on 5-(4′-nitrophenylazo) 25,27-bis(2-propyloxy) 26,28-dihydroxycalix[4] arene,

   P.S. Ramanjaneyulu, Parminder Singh, Y.S. Sayi, H.M. Chawla, K.L. Ramakumar, Journal of Hazardous Materials, 175 (2010) 1031-1036.
5. Estimation of Uncertainty in Measurement of Boron in Zr-Nb Alloy Samples by BF_4^- Ion Selective Electrode,

   P.S. Ramanjaneyulu, K.L. Ramakumar and Y.S. Sayi,

   Accrediation and Quality Assurance journal 15 (2010) 665-671.

6. Determination of boron in Zirconium – Niobium alloys by spectrophotometry,

   P.S. Ramanjaneyulu, Y.S. Sayi and K.L. Ramakumar,

   Indian Journal of Chemical Technology 17 (2010) 468-470.

7. A new Ion selective electrode for Cesium based on calix[4]arene crown-6compounds.

   P.S. Ramanjaneyulu, AbhaNaveen Kumar, Y.S. Sayi, K.L. Ramakumar, S.K. Nayak andS. Chattopadhyay,

   Journal of Hazardous Materials, 205-206 (2012) 81-88.

Technical Reports

1. Determination of Boron in Zirconium – Niobium Alloys by Spectrophotometry and BF_4^- ISE - Estimation of Expanded Uncertainty in Measurements,

   P.S. Ramanjaneyulu, Y.S. Sayi, K.L. Ramakumar,

   B.A.R.C. Report No., BARC/2009/R/003.

Conferences

1. Determination of Boron in Silicon Related Nuclear Materials by Spectrophotometry

   P.S. Ramanjaneyulu, Y.S. Sayi and K.L. Ramakumar

   Page No.477, Nuclear and Radiochemistry Symposium (NUCAR-07), Feb14-17, 2009. MS University, Vadodara, India

2. Determination of Boron in Zirconium – Niobium Alloys Spectrophotometry and BF_4^- ISE,

   P.S. Ramanjaneyulu, Y.S. Sayi and K.L. Ramakumar,

   Page no. 465, Nuclear and Radiochemistry Symposium (NUCAR-09), Jan 7-10, 2009. SVKM Mithibai College, Vile Parle, Mumbai.(Oral Presentation)

3. Development of Ion Selective Electrode for Cesium.,

   P.S. Ramanjaneyulu, Anil Boda, Y.S. sayi, K.L. Ramakumar, Parminder Singh, H.M. Chawla and K.L. Ramakumar,

   Page no. 461, Nuclear and Radiochemistry Symposium (NUCAR-09), Jan 7-10, 2009. SVKM Mithibai College, Vile Parle, Mumbai.

4. Development new ion selective electrode for cesium,

   P.S. Ramanjaneyulu, AbhaNaveen Kumar, Y.S. Sayi, K.L. Ramakumar, S.K. Nayak andS. Chattopadhyay,

   Page No.483, Nuclear and Radiochemistry Symposium (NUCAR-11), Feb 22-25, 2011, GITAM University, Visakhapatnam, India.