CHAPTER – 5

Development of Coated Graphite Gallium

Ion Selective Electrode
5.1 Introduction

Gallium finds application in nuclear as well as non-nuclear fields. Uranium rich Ga-U alloys and compounds are technologically important materials. Uranium rich GaU alloys have been found to show magnetic and electrical transport. Gallium/Indium compounds such as Gallium nitride, Gallium arsenide, Indium antimonide, Indium arsenide, Indium phosphide and Indium Gallium arsenide are extensively used in electronics industry as semiconducting materials. Gallium is also a component in low melting alloys to stabilise allotropes of plutonium and as heat exchanger in nuclear reactors. An alloy of In, Ag and Cd has been used in nuclear control rods. Due to high neutron absorption cross-section of In (270 barns), it has also added recently as one of the specification elements in nuclear fuels. Thus, in view of the importance of Gallium and Indium in many applications, it becomes imperative to analyse these elements in a variety of matrices. Gallium compounds (GaN, GaAs) are used as semiconductors, especially in light-emitting diodes, while the new photovoltaic compound, Cu(In,Ga)(Se,S)₂, is reported to be useful in solar panels as alternative to crystalline silicon. Gallium readily alloys with most metals, and is used as a component in low-melting alloys. In particular, it is used to stabilize the allotropes of plutonium. Ga-U and Ga-Pu systems have been studied for the development of new metal fuel reactors with respect to their thermodynamic stability for high temperature applications. Gallium is known to degrade the properties of many metallic materials via corrosion, embrittlement, or intermetallic phase formation. In view of these, sensitive and reliable methods for the determination of trace and minor concentrations of gallium are required.
Gallium is normally used for nuclear alloy fuels along with plutonium metal for strategic applications. However, plutonium has many allotrophic forms, ranging from alpha to epsilon [129]. Amongst these the delta phase is stable at 320° to 440°C and is important because of its desirable properties [130]. Alloying plutonium with a small amount of gallium (1–2%) stabilizes the delta phase of plutonium at room temperature and provides substantial corrosion protection in atmosphere [131] Pu-Ga alloy thus formed is found to be one of the alternate reference materials for plutonium. Accurate determination of gallium, therefore, forms an important part of the chemical characterization of this Pu-Ga alloy.

There are several methods available for the determination of gallium viz., spectrophotometry [132], chromatography [133], ICP-AES [134], ICP-MS [135], calorimetry [136], AAS [137], and polarography [138] etc. However these methods require expensive instruments, well-controlled experimental conditions. The use of electrochemical sensors on the other hand has the advantages of use of simple instruments, rapid and easy, applicable over concentration range from milligram to microgram, enhanced sensitivity and good selectivity. A few methods have been reported in the literature for the determination of gallium by potentiometry using ion selective electrode [139,140]. Many of these ion selective electrodes are prepared with organic ion-exchangers having large sized molecules and with neutral carriers. These membranes are sensitive to a large number of ions than the glass and solid state membranes. Among this Ca²⁺, K⁺ ion electrodes are commercially available. The need for the determination of many heavy metals in the environment has prompted the development of a number of different
ionophores. Since there are no investigations about gallium membrane electrodes prepared using Aliquat 336; the aim of this study was to construct, characterize and use some of them in potentiometric determination of gallium ions. Their optimum working conditions for the determination of gallium were investigated and the interference studies have been made. The selectivity coefficient of this electrode with respect to the different ions were determined by matched potential method. This electrode has been used for the determination of gallium ions using direct method. Prior to fabrication and use of gallium ion selective electrode, let us look into the various methods available for the determination of gallium in experimental solutions. However, the following methods can be adopted for the determination of gallium in Pu-Ga alloy type fuels only after the separation of plutonium from Pu-Ga solutions.

5.2 Methods for Determination of Gallium

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

5.2.1 Gravimetric Methods

Gravimetric methods involve precipitation of gallium as insoluble compounds of known composition and their determination as the stable Ga$_2$O$_3$. Some of the approaches used are given below.

(i) Precipitation with ammonium hydroxide [141]: Gallium was precipitated as Ga(OH)$_3$ by ammonium hydroxide. Excess of ammonia should be avoided as gallium hydroxide is soluble in NH$_4$OH.
(ii) **Precipitation with sulphite** [142,143]: Gallium is precipitated as Ga(OH)₃ by solid sodium sulphite or from aqueous solution of ammonium bisulphate. The precipitate is heated to above 813°C and weighed as Ga₂O₃.

(iii) **Precipitation with urea** [144,145]: Ga(OH)₃ is precipitated from dilute H₂SO₄ with urea followed by determination as Ga₂O₃ after hydrolytic decomposition of basic gallium sulphate at 475°C.

(iv) **Precipitation with aniline** [146]: Gallium is precipitated as Ga(OH)₃ by aniline from boiling solutions, heated to >550°C and determined as Ga₂O₃. The method was used for the determination of gallium in presence of iron.

(v) **Precipitation with pyridine in presence of NH₄Cl** [147]: Gallium was precipitated as gallium hydroxide with pyridine. Separation from alkali and alkaline earth metals was possible.

(vi) **Precipitation with cupferron (ammonium nitrosophenyl hydroxylamine)** [148]: The precipitate was ignited to oxide at temperature above 745°C. Fe(II) did not interfere. Gallium was determined in presence of many folds of aluminium by this method.

(vii) **Precipitation with camphoric acid** [149–151]: Gallium was precipitated quantitatively by camphoric acid or sodium camphorate. The precipitate was ignited and weighed as Ga₂O₃. Many metal ions did not interfere. Indium, iron(III) and aluminium (>10 mg) were found to interfere.

(viii) **Precipitation with 8-quinolinol or 5,7-dibromo-8-quinolinol** [152-154]: It was highly unspecific as many metal ions interfered.

(ix) **Precipitation with tannin (digallic acid)** [155]: Precipitation of gallium with tannin was used for its determination, but iron and aluminium were found to interfere.
Electrodeposition [156-157]: Gallium was deposited electrolytically on a platinum cathode from an alkaline solution in presence of hydrazine sulphate and was determined as metal. Platinum interfered by getting deposited on the cathode after anodic dissolution. Although gravimetric methods are convenient, they require large sample size (100 mg or more) for accurate determination in addition to inherent problems such as solubility of the precipitate, co-precipitation of other ions etc. Ga₂O₃ is also hygroscopic in nature. When gallium amount in the sample solution is small, gravimetric methods are unsuitable for its determination. Mass Spectrometry, Colorimetry, Flame Photometry, Fluorimetry, Emission Spectroscopy and Radiochemical methods are employed when gallium is present in a few micrograms.

5.2.2 Polarography

In acid solutions, the polarographic wave for gallium was observed very close to the reduction wave of hydrogen [158]. This made the polarographic determination of gallium rather difficult. According to Vinogradova and Chudinova [159], in salicylate solution (>0.003M) at pH 2.8 to 3.4, gallium gave an irreversible wave with a half-wave potential of ~0.88V vs. S.C.E., the wave height was proportional to gallium concentration in the range of 0.028 to 0.0014 M.

5.2.3 Colorimetric Methods

Absorptiometric and fluorimetric methods were reported for gallium determination with Rhodamine B [160-162]. Rhodamine B chlorogallate was extracted into chlorobenzene – carbon tetrachloride mixture after adding TiCl₃.
to suppress the reagent blank. One to 10 µg of Ga was determined with an error of 5 to 10%.

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

### 5.2.4 Fluorimetric Methods [164-166]

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

Rhodamine B chlorogallate extract in benzene was used for the fluorimetric determination of 0.2 to 2.0 µg of Ga.

### 5.2.5 Flame Photometry

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

### 5.2.6 Mass Spectrometry

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

5.2.7 Spectrophotometric Methods

Phenylfluorone reacts with Ga(III) in presence of hexadecylpyridinium bromide and pyridine to form a water-soluble chelate with an absorption maximum at 570 nm in pH range of 4.0 to 5.5 [170]. At this wavelength the Beer’s law is obeyed upto $4.3 \times 10^{-5}$ M Ga. The method has high sensitivity and can be used for Ga determination at microgram level.

5.2.8 Radiochemical Methods

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

5.2.9 Titrimetric Methods [171-205]

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

5.3 Determination of Gallium using EDTA as a Titrant

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

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

5.3.1 **Titration with Potassium Ferrocyanide**

Potassium ferrocyanide forms compounds with many metal ions due to its strong complexing ability. Since the ferricyanide-ferrocyanide system is reversible, it was used as a redox titrant for many metal ions. End point of such titration was detected either with the help of redox indicators, or by electroanalytical methods like potentiometry or amperometry. Kirschman and Ramsey and Ato studied the potentiometric titration of gallium with standard potassium ferrocyanide solution containing potassium ferricyanide. In 0.0015 to 0.005N HCl, the composition of the precipitate formed corresponded to the formula Ga₄[Fe(CN)₆]₃. Ato determined 5 to 20 mg of Ga while Kirschman and Ramsey titrated 33 to 130 mg of Ga.
The use of dead-stop end point (biamperometry) in the titration of 0.05 to 0.17 millimoles of gallium with a standard potassium ferrocyanide solution was reported. The optimum conditions for the experiments were pH of 2.0 and temperature of 50°C, when the potential difference across the Pt wire electrodes was 230 mV. Chloride, sulphate and perchlorate ions did not interfere, while presence of ammonium ions gave slightly high results.

Belcher proposed the use of redox indicators like 3,3’-dimethyl naphthidine and / or 3,3’-dimethyl naphthidine disulphonic acid in the titration with K₄Fe(CN)₆ in presence of small amounts of K₃Fe(CN)₆ and determined 0.74 to 2.94 mg of Ga with uncertainty of ± 0.25%.

5.3.2 Titration with Potassium Bromate

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

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

Coated graphite Gallium ion selective electrode was developed by depositing a membrane comprising of Aliquat-336 loaded with Gallium in the form GaCl₄⁻ and poly vinyl chloride in the ratio of 70:30. Specific properties of the electrodes were studied including calibration curve, slope, detection limit, concentration range, response time and life time. The effect of chloride concentration was investigated. This coated graphite Gallium ion selective
electrode exhibits linear Nernstian response over gallium concentration range of 1x10^{-4} M-1x10^{-1} M of Ga(III) ions in constant chloride concentration of 6M with a detection limit of 2x10^{-5} M calibration slope of -58.2 mV ± 1.0 mV/decade change in concentration of Ga. Interference of Li^{+}, Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Fe^{3+}, Cr^{3+}, Ni^{3+}, Th^{4+}, U(VI), OH^{-}, CO_{3}^{2-} and NO_{3}^{-} on electrode response have also been investigated. The selectivity coefficients of this electrode with respect to the different ions were determined by matched potential method. This coated graphite gallium ion selective electrode can be used for consecutive three months without losing Nernstian response.

5.4.1 Experimental

5.4.1.1 Reagents employed

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

5.4.1.2 Instruments used

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

5.4.1.3 Preparation of Ga stock solution

Stock solution of Gallium in 7M HCl was prepared by dissolving 99.99% pure gallium metal in a mixture of concentrated HCl and HNO_{3} and the nitrate was
evaporated almost to dryness using conc. hydrochloric acid. The residue gallium chloride in the form of \( \text{GaCl}_4^- \) was then dissolved in 7M HCl and made up to a known concentration.

5.4.1.4 Loading of Aliquat 336 with Gallium

About 2-3 ml Aliquat 336 (in chloride form) was equilibrated with 5 ml of Gallium Stock solution. The mixture was stirred on a magnetic stirrer for about 5 hours and allowed to settle overnight. The organic phase containing Aliquat 336 loaded with \( \text{GaCl}_4^- \) was separated and used for preparation of ion selective electrodes using spectroscopy pure graphite rod. The amount of gallium loaded on Aliquat-336 was ~300mg/ml.

5.4.1.5 Construction of Electrode

Coated graphite gallium ion selective electrode was prepared using the technique as reported in the literature. The spectroscopic grade high purity graphite rod (5 mm OD and 100 mm length) was taken and the central portion of the rod was encapsulated in a glass tube such that one end of the electrode could be used for membrane coating and the other end for emf measurements. The membrane coating methodology consisted of mixing required weighed amounts of the Aliquat 336 loaded with \( \text{GaCl}_4^- \) and PVC in the suitable amount of solvent namely Tetrahydrofuran (THF). One end of the graphite rod was repeatedly dipped into this mixture until a uniform, adhesive coating was obtained on the graphite rod. The electrodes were then dried in air for 48 hours. Gallium ion selective electrodes having different membrane composition i.e. with Aliquat 336: PVC in the ratio of 80:20, 70:30 and 60:40 were prepared for optimizing the electrode composition. The coated graphite gallium ion selective electrode was conditioned at least for one hour in

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1M Gallium solution prior to analysis.

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

\[ 4R_3N+\text{CH}_3\text{Cl} (\text{org}) + \text{GaCl}_4^- (\text{aq}) \rightarrow (R_3\text{NCH}_3)_4\text{GaCl}_4(\text{org}) + 4\text{Cl}^- (\text{aq}) \]  

5.4.1.6 Preparation of Standard Solutions

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

5.4.1.7 EMF Measurements

To measure the potential of the standard/test solution, about 10 ml of Ga sample solution was taken in a beaker. Ga ion selective electrode and double junction reference electrode were dipped in the solution and EMF of the cell was measured using 4-star Orion ion meter. Care was taken that during all the measurements entire coated part of the electrode was immersed in the solution. The solution was continuously stirred before the measurement was done. This Gallium ion selective electrode was conditioned by soaking in $1\times10^{-1}$ M Ga solution prior to use. The salt bridge solution namely saturated KCl (primary junction) and 5.5M LiCl+0.5M HCl mixture (secondary junction) were regularly changed in the reference electrode before emf measurements.

5.4.2 Results and Discussion

5.4.2.1 Calibration Curve for Coated Graphite Ga-ISE

Figure 5.1 shows the calibration curve of coated graphite gallium ion selective electrode. It was shown that the electrode was responding satisfactorily to the
gallium standard solutions in the range from $1 \times 10^{-4}$ M to $1 \times 10^{-1}$ M. The response behavior of the electrode was found not to change significantly with time, which would not affect the analytical results when fresh calibration is employed for measurements. Hence it can be seen that this electrode can be used with fair amount of reproducibility.

![Graph showing calibration curve](image)

**Figure 5.1** Calibration Curve of Coated Graphite Ga-ISE

### 5.4.2.2 Optimization of Electrode Composition

**Figure 5.2** shows the responses of gallium ion selective electrodes in different ratios of Aliquat 336 loaded with GaCl$_4^-$ and PVC viz. 80:20, 70:30 and 60:40. It can be seen that the gallium ion selective electrode in the ratio of 70:30 gave better slope ($S = -58.2$) than the other compositions viz. 80:20 ($S = -56.6$); 60:40 ($S = -55.5$) and hence the composition 70:30 was employed for all the subsequent studies. The ratio of 90:10 did not yield a suitable membrane for
studies and the ratio of 50:50 was found to be giving unstable reading during emf measurements and hence was not employed in this study.

**Figure 5.2** Optimization of electrode composition using GaCl$_4^-$ loaded Aliquat 336 and PVC

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

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

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

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

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

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

$$\text{Selectivity Coefficient} = \frac{\Delta a_A}{a_B}$$  \hspace{1cm} 5.1

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

5.4.2.5 Interference Studies due to Cationic Impurities

Interference in presence of Na^+, K^+, Ca^{2+}, Ba^{2+}, Mg^{2+}, Fe^{3+}, Cr^{3+}, Ni^{3+}, Th^{4+} and U(VI) ions on the potential measurement of gallium solution using coated
graphite gallium ion selective electrode of a typical membrane composition of 70% Aliquat-336 loaded with GaCl$_4^-$, 30% PVC was investigated by adopting matched potential method. The potential of the solution containing constant initial concentration (1x10$^{-4}$M) of primary ion i.e. Gallium, was varied by about 30 mV in four to five increments either by adding gallium standard solution or impurity ion solution prepared in 6M Cl$^-$. The selectivity coefficient obtained from these studies is summarized in Table 5.1. The results clearly showed that the impurity ions studied have negligible interference in gallium measurement.

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

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Impurity ion</th>
<th>Selectivity Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na(I)</td>
<td>2.26 x 10$^{-3}$</td>
</tr>
<tr>
<td>2</td>
<td>K(I)</td>
<td>3.18 x 10$^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>Ca(II)</td>
<td>4.75 x 10$^{-4}$</td>
</tr>
<tr>
<td>4</td>
<td>Ba(II)</td>
<td>2.31 x 10$^{-3}$</td>
</tr>
<tr>
<td>5</td>
<td>Mg(II)</td>
<td>3.23 x 10$^{-3}$</td>
</tr>
<tr>
<td>6</td>
<td>Fe(III)</td>
<td>3.86 x 10$^{-2}$</td>
</tr>
<tr>
<td>7</td>
<td>Cr(III)</td>
<td>1.43 x 10$^{-2}$</td>
</tr>
<tr>
<td>8</td>
<td>Ni(III)</td>
<td>4.52 x 10$^{-3}$</td>
</tr>
<tr>
<td>9</td>
<td>Th(IV)</td>
<td>2.47 x 10$^{-3}$</td>
</tr>
<tr>
<td>10</td>
<td>U(VI)</td>
<td>2.73 x 10$^{-2}$</td>
</tr>
</tbody>
</table>
5.4.2.6 Interference due to Anionic Impurities

Since the present work involves measurement of anionic complex of gallium, the presence of various anionic impurities viz., OH\(^-\), CO\(_3\)\(^{2-}\), NO\(_3\)\(^-\) ions were also investigated. It was observed that there was no significant interference due to the presence of above anionic impurities during the determination of gallium. The results are tabulated in Table 5.2.

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

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Impurity ion</th>
<th>Selectivity Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OH(^-)</td>
<td>2.83 x 10(^{-3})</td>
</tr>
<tr>
<td>2</td>
<td>CO(_3)(^{2-})</td>
<td>4.32 x 10(^{-3})</td>
</tr>
<tr>
<td>3</td>
<td>NO(_3)(^-)</td>
<td>3.89 x 10(^{-3})</td>
</tr>
</tbody>
</table>

5.4.2.7 Response of Ga-ISE

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

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values / range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimized Membrane Composition</td>
<td>Aliquat 336 loaded with GaCl$_4^-$ : PVC (70:30)</td>
</tr>
<tr>
<td>Electrode type</td>
<td>Coated graphite Gallium ion selective electrode</td>
</tr>
<tr>
<td>Electrolyte medium (6M Cl$^-$)</td>
<td>5.5M LiCl+0.5M HCl for all standards and samples</td>
</tr>
<tr>
<td>Conditioning time</td>
<td>One hour prior to use</td>
</tr>
<tr>
<td>Linear range (M)</td>
<td>1x10$^{-4}$ – 1x10$^{-1}$</td>
</tr>
<tr>
<td>Slope (mV/decade)</td>
<td>-58.2 ± 1.0</td>
</tr>
<tr>
<td>Detection Limit</td>
<td>2.0x10$^{-5}$M</td>
</tr>
<tr>
<td>Response time</td>
<td>&lt; 100 seconds</td>
</tr>
</tbody>
</table>

### 5.4.2.8 Life Time of Ga-ISE

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

Figure 5.7 Lifetime of Ga-ISE

5.4.2.9 Analytical Application of Ga-ISE

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coated Graphite (*) Gallium ISE (µg/ml)</th>
<th>Expected (µg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCS-CRM 346 Nickel Alloy IN 100</td>
<td>49.7±0.99</td>
<td>50.60±1.01</td>
</tr>
</tbody>
</table>

[ (*) Results based on triplicate measurements]

5.4.3 Storage of Coated Graphite Ga-ISE

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

5.4.4 Conclusion

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