Available online at
www.ijacskros.com

Indian
Journal of Advances in
Chemical Science

Indian Journal of Advances in Chemical Science 2 (2) (2014) 110-115

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

R. Govindan[1]*, D. Alamelu[2], S.C. Parida[1], A.R. Joshi[1]

[1]Product Development Division, Bhabha Atomic Research Centre, Mumbai-400 085, India
[2]Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai-400 085, India
Received 14th February 2014; Accepted 17th February 2014.

ABSTRACT

Coated graphite Gallium ion selective electrode was developed by depositing a membrane comprising of Aliquat-336 loaded with Gallium in the form $GaCl_4^-$ *and poly vinyl chloride in the ratio of 70:30. Specific properties of the electrodes were studied including calibration curve, slope, detection limit, concentration range, response time and life time. The effect of chloride concentration was investigated. This coated graphite Gallium ion selective electrode exhibits linear Nernstian response over gallium concentration range of* $1x10^{-4}M - 1x10^{-1}M$ *of Ga(III) ions in constant chloride concentration of 6M with a detection limit of* $2x10^{-5}$ *M calibration slope of -58.2 mV ± 1.0 mV/decade change in concentration of Ga. Interference of* Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Fe^{3+}, Cr^{3+}, Ni^{3+}, Th^{4+}, *U(VI),* OH^-, CO_3^{2-} *and* NO_3^- *on electrode response have also been investigated. The selectivity coefficients of this electrode with respect to the different ions were determined by matched potential method. This coated graphite gallium ion selective electrode can be used for consecutive three months without losing Nernstian response.*

Keywords: *Gallium ion selective electrode; coated graphite electrode; Aliquat 336; ion selective electrode; gallium determination*

1. INTRODUCTION

The use of ion selective electrodes for analytical purposes has been growing fast since last three decades. The increasing number of investigations about ion selective electrodes has been done because of their ease in use and their selectivity characteristics. This analytical technique provides accurate, rapid and cost effective method of analysis. There are several methods available for the determination of gallium viz., spectrophotometry [1], chromatography[2], ICP-AES[3], ICP-MS[4], calorimetry[5], AAS[6], and polarography[7] 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 [8,9]. Many of these ion selective electrodes are prepared with organic ion-exchangers having large sized molecules and with neutral carriers. These membranes are sensitive to a large number of ions than the glass and solid state membranes. Among this Ca^{2+}, K^+ ion electrodes are commercially available. The need for the determination of many heavy metals in the environment has prompted the development of a number of different ionophores. Since there are no investigations about gallium membrane electrodes prepared using Aliquat 336; the aim of this study was to construct, characterize and use some of them in potentiometric determination of gallium ions. Their optimum working conditions for the determination of gallium were investigated. Interference studies have been made. The selectivity coefficients 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. This paper describes development of coated graphite Gallium ion selective electrode for the direct determination of gallium in experimental solutions.

2. EXPERIMENTAL

2.1. Reagents Employed

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

---

*Corresponding Author:
Email: rgovindan66@gmail.com
Phone: +91 22 2559 5647 / 2559 4790

2.2. 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.

2.3. 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 $GaCl_4^-$ was then dissolved in 7M HCl and made up to a known concentration.

2.4. Loading of Aliquat 336 with Gallium

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

2.5. Construction of Electrode

Coated graphite gallium ion selective electrode was prepared using the technique as reported in the literature[10]. The spectroscopic grade high purity graphite rod (5mm OD and 100mm length) was taken and the central portion of the rod was encapsulated in a glass tube such that one end of the electrode could be used for membrane coating and the other end for emf measurements. The membrane coating methodology consisted of mixing required weighed amounts of the Aliquat 336 loaded with $GaCl_4^-$ 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 10^{-1}M Gallium solution prior to analysis.

2.6. 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.

2.7. EMF Measurements

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

3. RESULTS AND DISCUSSION

3.1. Calibration Curve for Coated Graphite Ga-ISE

Figure 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 $1x10^{-4}$ M to $1x10^{-1}$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.

3.2. Optimization of Electrode Composition

Figure 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.

3.3. 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 3 shows the study of various

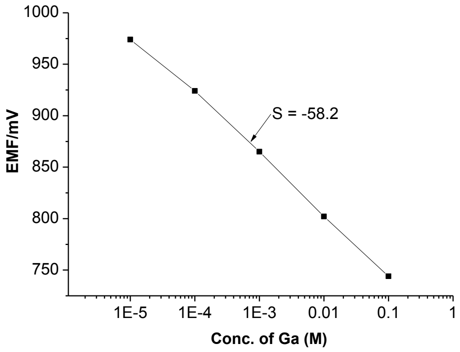

Figure 1 Calibration Curve of Coated Graphite Ga-ISE.

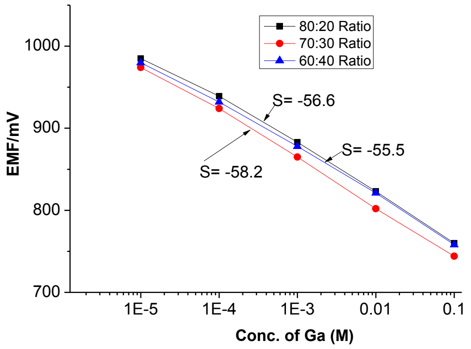

Figure 2 Optimization of electrode composition using $GaCl_4^-$ loaded Aliquat 336 and PVC.

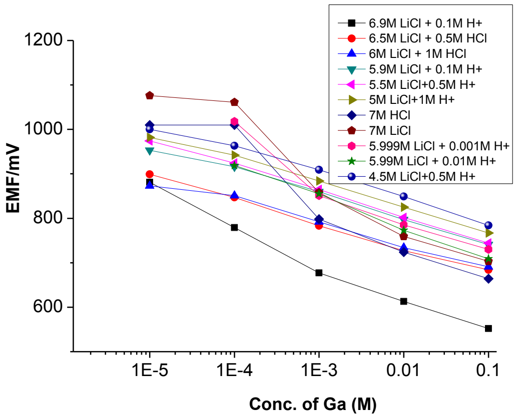

Figure 3 Study of Electrolyte Composition using LiCl or HCl or mixture of LiCl+HCl (Cl^- Conc.: 5 M, 6 M, 7 M).

Figure 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.

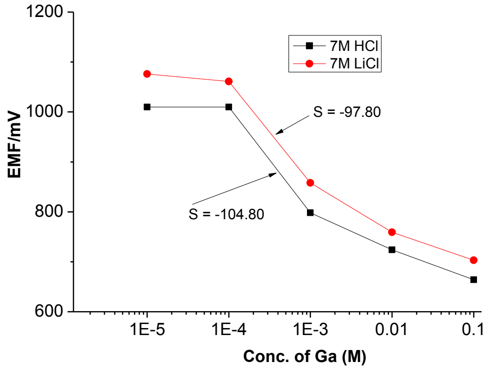

Figure 4 Calibration Curve at Chloride Concentration 7M (HCl or LiCL).

Similar studies were carried out by using mixture of LiCl and HCl at varying compositions viz., at 5 M, 6 M and 7 M (Figure 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 (6.5 M+0.5 M [S= -55]; 5.9M+0.1 M [S= -54.3]; 5 M+1 M [S= -54.7] and 4.5 M+0.5 M [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.

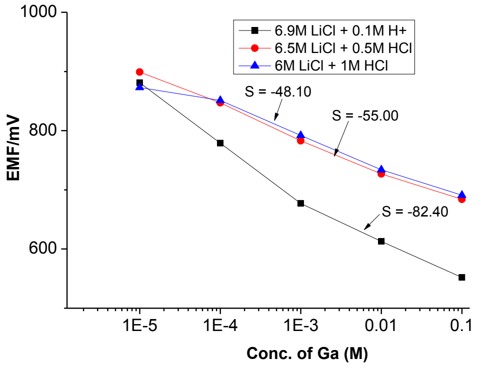

Figure 5 Calibration Curve at Chloride Concentration 7M (LiCl+HCl).

3.3. 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)[11-13]. In this method, 5 mL of 1 x 10^{-4} M Ga in 0.5 M HCl + 5.5 M 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 (Δa_A) was calculated. In the second set of experiments, potential of 5 mL of 1x10^{-4} M gallium in 0.5 M HCl+5.5 M LiCl was varied in similar increments by addition of standard solution of impurity ion (a_B) prepared in 0.1 M 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 (Δa_A) and concentration of impurity ion (a_B) required to carry out the same change in potential, selectivity coefficients were calculated as follows:

$$\textit{Selectivity Coefficient} = \Delta a_A / a_B$$

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

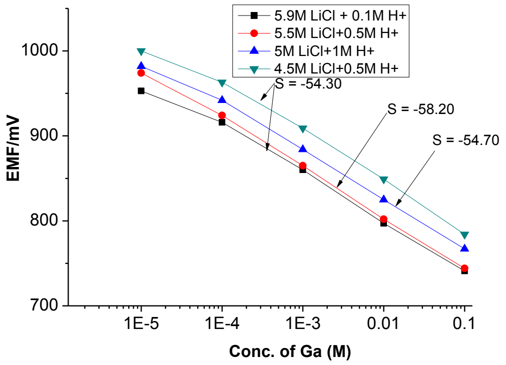

Figure 6 Calibration Curve at Chloride Concentration 6M / 5M (LiCl+HCl).

3.4. 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 6 M Cl^-. The selectivity coefficient obtained from these studies is summarized in Table 1. The results clearly showed that the impurity ions studied have negligible interference in gallium measurement.

Table 1 Selectivity coefficient of cationic impurities using coated wire Uranyl ISE.

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

3.5. 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 2.

Table 2 Selectivity coefficient of anionic impurities using coated wire Urayl ISE.

S.No.	**Impurity ion**	**Selectivity Coefficient**
1	OH^-	2.83 x 10^{-3}
2	CO_3^{2-}	4.32 x 10^{-3}
3	NO_3^-	3.89 x 10^{-3}

3.6. 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 3.

3.7. Life Time of Ga-ISE

The gallium ion selective electrode was calibrated almost every day and it can be seen from the Figure 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^o value

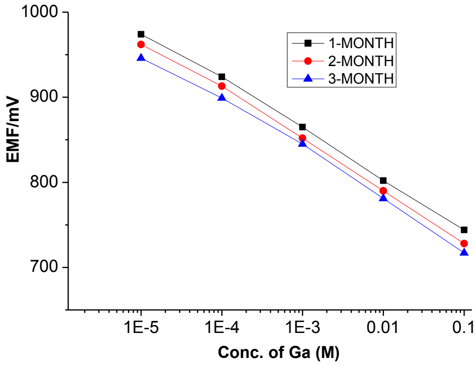

Figure 7 Lifetime of Ga-ISE.

Table 3. Response characteristics of the coated graphite gallium ion selective electrode.

Properties	Values / range
Optimized Membrane Composition	Aliquat 336 loaded with $GaCl_4^-$: PVC (70:30)
Electrode type	Coated graphite Gallium ion selective electrode
Electrolyte medium (6M Cl^-)	5.5M LiCl+0.5M HCl for all standards and samples
Conditioning time	One hour prior to use
Linear range (M)	$1x10^{-4} – 1x10^{-1}$
Slope (mV/decade)	-58.2 ± 1.0
Detection Limit	$2.0x10^{-5}$M
Response time	< 100 seconds

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.

3.8.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 and for BCS-CRM 345 Nickel Alloy IN 100 the specification of Ga is 8.2 ppm.

3.9. 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.

4. CONCLUSION

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

Acknowledgments - Authors are grateful to Dr. K. L. Ramakumar, Director, RC and I Group, BARC for his valuable guidance and constant encouragement during the course of this work.

5. REFERENCES

[1]. Z. Marczenko, H. Kalowska, (1979) Sensitive Spectrophotometric Determination of Gallium with Eriochrome Cyanine R and Cetyltrimethylammonium ions, ***MicrochimicaActa [Wien],*** II:507-514.

[2]. M. S. Gidwani, S. K. Menon, Y. K. Agrawal, (2002) Chelating polycalixarene for the chromatographic separation of Ga(III), In(III) and Tl(III),***Reactive and Functional Polymers,*** **53,** 143-156.

[3]. H. F. Koch, L. A. Girard, D. M. Roundhill, (1999) Determination of Gallium in a Cerium Surrogate and in Drops from a Copper Collector by ICP as Model Studies for the Removal of Gallium from Plutonium, ***Atomic Spectroscopy,*****20,** 30-32.

[4]. M. Martin, F. X. Olivier, (1998)Simultaneous Determination of Volatile Metal (Pb, Hg, Sn, In, Ga) and Nonmetal Species (Se, P, As) in Different Atmospheres by Cryofocusing and Detection by ICPMS. ***Analytical Chemistry,*****70,** 2639-2645.

[5]. C. G. S. Queiroz, M. L. Guia, A. C. Magalh, (2000) Microcalorimetric evaluation of metabolic heat rates in coffee (Coffeaarabica L.) roots of seedlings subjected to chilling stress. ***Thermochimica Acta,*** **351,** 33-37.

[6]. H. Tanaka, A. Mitani, K. Okamoto, H. Morita, S. Shimomura, (1997), Determination of gallium by AAS using tantalum carbide-coated graphite tube, ***Bunseki Kagaku,*** **46**(11), 875:880.

[7]. S. Puri, R. K. Dubey, M. K. Gupta, B. K. Puri, (1998)Differential Pulse Polarographic Determination of Gallium and Niobium in Samples After Preconcentration of Their Quinolin-8-Olate Complexes on Microcrystalline Naphthalene. ***Analytical Letters,*** **31,** 841-857.

[8]. N. Yoshikuni, H. Takeno, K. Oguma,(2001) Preparation of Gallium ion selective electrode by use of anion-exchange resin and its application to chemical analysis of industrial

materials. ***Bunseki Kagaku Abstracts,*** **50**(11), 753-757.

[9]. K. Sabry. Mohamed, (2006)Ion-selective electrode for gallium determination in nickel alloy, fly-ash and biological samples. ***Analytica Chimica Acta,*** **562**, 204-209.

[10]. R. W. Cattrall, C. PohPul,(1975) Coated Wire Ion Selective Electrode for the Determination of Iron(III), ***Analytical Chemistry***, **47**, 93-95.

[11]. G. Horvai, (1997) The matched potential method, a generic approach to characterize the differential selectivity of chemical sensors, ***Sensors and Actuators***, *B*, **43**, 94-98.

[12]. V.P.Y.Gadzekpo, G.Christian, (1984) Determination of selectivity coefficients of ion selective electrodes by a matched-potential method, ***AnalyticaChimicaActa***, **164**:279-282.

[13]. Yoshio Umezawa, Kayoko Umezawa and Hitoshi Sato,(1995) Selectivity Coefficients for Ion-Selective Electrode Electrodes - Recommended Methods for Reporting $K_{A,B}^{pot}$ values. ***Pure and Applied Chemistry***, **67**: 507-518.