



Determination of Lithium in Organic Matrix Using Coated Wire Lithium Ion Selective Electrode

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ABSTRACT

Coated wire lithium ion selective electrode was fabricated using lithium ionophore-VI, 2-nitrophenyl octyl ether (NPOE) and potassium tetrakis(p-chlorophenyl)borate (KTPClPB) on platinum wire. Lithium ion selective electrode was giving Nernstian response from $10^{-1}M$ to $10^{-4}M$ with a detection limit of $3 \times 10^{-5}M$. The calibration slope of this lithium ion selective electrode was found to be 58.5 ± 1.0 mV/decade. The selectivity coefficients of this electrode with respect to the different ions were determined by matched potential method. This lithium ion selective electrode was then used for the determination of lithium in complex chemical matrix containing hexamethylene tetramine, formaldehyde, urea and ammonium nitrate etc. which are the wash streams generated during the sol-gel process employed for preparation of Li_2TiO_3 microspheres.

Keywords: Lithium ion selective electrode; coated wire electrode; ion selective electrode; Aliquat 336; lithium determination; HMTA; organic matrix.

1. INTRODUCTION

There are many literatures available on Lithium ion selective electrode [1-6] which are mostly used in a pharmaceutical line for the determination of lithium in serum blood. Recently, Lithium ion selective electrode was employed to measure the cardiac output of the patients in intensive care using lithium dilution method [7]. Most of these lithium ion selective electrodes are liquid membrane based electrodes and are being used selectively for the determination of lithium in serum blood. The application of these electrodes to determination of lithium in organic matrix is restricted. In addition, the fabrication of these ion selective electrodes is cumbersome as the preparation of this ionophore involved many steps and not suitable for the determination of lithium in organic matrix. Moreover these ion selective electrodes should be properly maintained unless the current coated wire lithium ion selective electrode can be kept dry in air. So far, there is no literature available for the determination of lithium in samples containing complex chemical mixture using coated wire lithium ion selective electrode. A method has been developed for the determination of lithium by potentiometry using commercially available fluoride ion selective electrode by the current author [8]. This method involved the determination of lithium by "indirect method" by potentiometric titration using fluoride ion selective electrode. This method is time consuming in obtaining the end

point during the titration of samples using 0.5M NH_4OH . Moreover the result could be obtained only after plotting the graph through Origin software for the detection of end point. Coated wire lithium ion selective electrode (Li-ISE) is exclusively developed for the determination of lithium in complex chemical mixture containing hexamethylene tetramine, formaldehyde, urea and ammonium nitrate etc. which are the wash streams generated in the sol-gel process employed for preparation of Li_2TiO_3 microspheres. The "novelty" of this method lies in the "direct method" of analyzing "lithium in organic matrix" after suitable treatment of synthetic / unknown samples. In addition, this method is very fast, cost effective, require no extra reagent and more reliable as compared to the other methods. The most important advantage of this method of lithium determination using coated wire lithium ion selective electrode is that it will be exclusively used for the determination of enriched lithium samples in future.

Lithium isotope (6Li) plays an important role in nuclear industry for the production of tritium during nuclear fusion reaction. The proposed fuel for fusion reactor is based on lithium-6 in which 6Li fuel would generate tritium by the following ${}^6Li(n,\alpha)T$ nuclear reaction inside the blanket of the thermonuclear reactor by exploiting the fast

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neutrons (n) coming from the D-T fusion reaction. Sol-Gel process is being used for the fabrication of nuclear fuel materials such as UO_2 [9,10] as well as non-nuclear materials in the form of microspheres (pebbles). Recently Li based ceramics viz., Li_2O , Li_2SO_4 , Li_2TiO_3 , Li_2SiO_3 , Li_2ZrO_3 [11] have received considerable importance as tritium breeders in Test Blanket Modules (TBMs) for fusion reactors based on D-T reaction. [12,13]. Lithium titanate (Li_2TiO_3) is considered as one of the best candidates for blanket in international thermonuclear experimental reactor (ITER) due to the properties like high efficiency of tritium production, high chemical and mechanical stability and good tritium release was prepared in the form of pebbles by internal gelation technique of sol-gel process.

Presently, studies are being carried out using natural lithium in these materials. Li_2O is promising for obtaining suitable tritium breeding ratio (TBR) [14] but not used because of its high sensitivity towards moisture whereas lithium meta-titanate (Li_2TiO_3) was proposed as an important material for TBM because of its good chemical stability and possibility of tritium recovery at relatively low temperature [15]. Sol-gel process was hence developed for the preparation of lithium containing ceramic materials in the form of pebbles of required size and characteristics as well as with the required Li:Ti stoichiometry [16]. Thus it was essential to determine lithium in wash solutions at various lots of preparation of lithium meta-titanate (Li_2TiO_3). The experiments were initially carried out using natural lithium for the preparation of lithium meta-titanate (Li_2TiO_3) by sol-gel team. In the Sol-Gel process, the Gel particle is actually made of Ti-hydroxide network in which lithium ion is trapped. During the preparation of Li_2TiO_3 (with enriched ^6Li) by sol-gel process, the microspheres are washed with ^6Li containing organic mixture ($\text{NH}_4\text{NO}_3 + \text{NH}_4\text{Cl} + \text{HMTA} + \text{Urea} + \text{LiOH}$) so that leaching of ^6Li from the sol-gel particles during washing can be minimized. The concentration of Li^+ needs to be optimum in the Gel so that the ultimate product is stoichiometric Li_2TiO_3 . The gel particle once produced was washed with LiOH containing organic solution to remove un-reacted and unused materials, while maintaining Li/Ti stoichiometry in gel. The number of washings required need be standardized so that the lithium concentration in gel does not deviate from the expected value. The washed solutions which contain enriched ^6Li also needed to be analyzed for lithium content prior to the recovery process. Thus the method required a simple and robust technique, which is capable of lithium determination to standardize the various steps of the sol-gel process. Determination of lithium in a complex chemical mixture containing HMTA, urea etc. by the

conventionally used techniques such as ICPMS, ICP-OES, TXRF etc., requires removal of organics. It was therefore considered worthwhile to investigate the possibility of determination of lithium using coated wire lithium ion selective electrode.

In the present work, the fabrication of coated wire lithium ion selective electrode, calibration, interference studies, lifetime of the electrode and its application to the analysis of lithium in complex organic matrix are demonstrated. The method adopted for the determination of lithium using coated wire lithium ion selective electrode in the various process streams generated during Li_2TiO_3 preparation where significant amount of organic constituents are present along with lithium. The lithium concentration data in the wash streams was obtained by coated lithium ion selective electrode was found to be within 2%.

2. EXPERIMENTAL

2.1. Regents / Instruments Required

Lithium ionophore (VI), Fluka Make, Poly(vinyl chloride) (PVC), Fluka Make, A.R. Grade 2-nitrophenyl octyl ether (NPOE), A.R. Grade potassium tetrakis (*p*-chlorophenyl) borate (KTpCIPB), A.R. Grade Anhydrous LiCl, A.R. Grade Anhydrous LiOH, A.R. Grade Anhydrous LiNO_3 , A.R. Grade Urea, A.R. Grade Hexamethylene tetramine. Double distilled water was used for the preparation of all reagents and standards. Orion 5-Star ion analyzer was employed to measure the potential developed using lithium ion selective electrode and double junction calomel reference electrode during the analysis. A magnetic stirrer was employed throughout the experiment for continuous stirring of the electrolytic solution during analysis.

2.2 Preparation of Li^+ Standards

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

2.3 Loading of LiCl on Lithium Ionophore (Vi) and Construction of Li-ISE

Initially, 29.6 mg of commercially available lithium ionophore (VI) was dissolved in 5 ml 2-nitrophenyl octyl ether (NPOE). To this 2.5 ml of 5M lithium chloride was added and equilibrated for one hour and the organic mixture was allowed to settle for few hours. The organic layer containing lithium was then separated from aqueous solution. Then, 300 mg of Poly(vinyl chloride) was dissolved in 2-3 ml Tetrahydrofuran. To this ~700 mg of organic mixture containing lithium ionophore (VI), NPOE

loaded with lithium chloride having ~5 mg of potassium tetrakis (*p*-chlorophenyl) borate (KTPCIPB) as an additive was mixed thoroughly using magnetic stirrer till slurry is formed. Then using Pt-wire (the central portion of the Pt-wire was encapsulated using glass tube) such that one end was used for membrane coating and the other end was used for electrical contact. This slurry was coated on the Pt-wire and the electrode was allowed to dry for two days (**Figure 1**). The lithium ion selective electrode was conditioned in 0.1M LiCl for few hours prior to analysis.

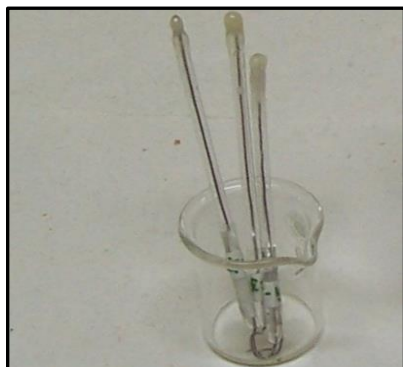


Figure 1. Coated wire Li-ion selective electrode.

2.4 Preparation of Lithium Titanate Microspheres

The lithium titanate microspheres were obtained by the internal gelation process [15]. Natural lithium nitrate and titanium chloride solutions were mixed with 3M solution containing a mixture of HMTA/urea at 0 °C to obtain feed solution. This feed solution was then dispersed as droplets through a stainless steel capillary of 0.8 to 1.0 mm internal diameter into a glass column in which hot silicone oil pre-heated to 90 °C was circulated. These droplets get hardened (gelled microspheres) as they travel down the column. The gelled microspheres were separated from oil, washed initially with CCl₄ (4 to 5 times), to remove the adhering silicone oil, dried and then digested in 1.55 M LiOH at 60°C in an air oven for 16 to 18 h. Washing with 1.55 M LiOH was done 6 to 7 times to remove the reaction products and unused chemicals from the microspheres to prevent their cracking during sintering. The microspheres were then dried at 100 °C. In order to study the pickup/leaching of lithium from the microspheres during the washing, LiOH used for washing was prepared from depleted ⁶Li. During the preparation of Li₂TiO₃ (with enriched ⁶Li) by sol-gel process, the microspheres are washed with ⁶Li containing organic mixture (0.54M NH₄NO₃+0.24M NH₄Cl+0.075M HMTA + 0.075M Urea + LiOH) so that leaching of ⁶Li from the sol-gel particles during washing can be minimized.

3. RESULTS AND DISCUSSION

3.1 Calibration Curve for Li ISE

Figure 2 shows the calibration curve of lithium ion selective electrode and it has been observed that the lithium ion selective electrode was responding satisfactorily to the lithium standard solutions in the range 1x10⁻⁴ M to 1x10⁻¹M with a detection limit of 3 x10⁻⁵ M. The calibration slope (S) of this lithium ion selective electrode was found to be 58.5 ± 1.0 mV/decade. The response behavior of the electrode was found not to change significantly with time, which would not affect the analytical results when fresh calibration is employed for measurements. Hence it can be seen that the electrode can be used with fair amount of reproducibility.

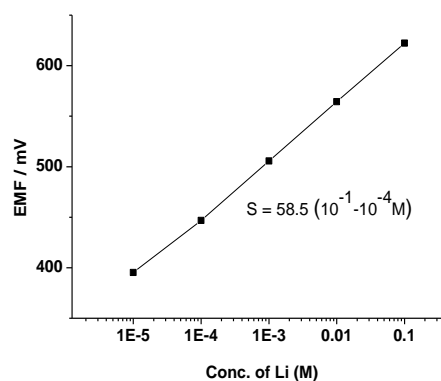


Figure 2 Calibration curve of lithium ion selective electrode.

The integrity of the electrode was tested with various lithium salts as the same will be used as a feed material for the preparation of lithium titanate microspheres. **Figure 3** shows the calibration curve for different lithium salts viz., LiOH, LiNO₃ and LiCl were plotted using lithium ion selective electrode. The slope of the lithium ion selective electrode in all the three salts was well within the

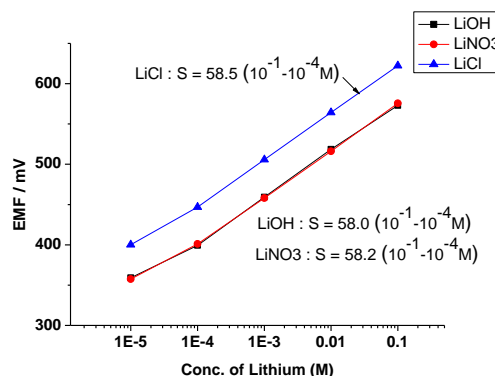


Figure 3 Calibration curves for different lithium salts.

3.2 Potentiometric Selectivity

The influence of interfering ions on the response behavior of ion selective electrodes is usually described in terms of selectivity coefficients. The selectivity coefficients for lithium with respect to

variety of interfering ions were described by matched potential method (MPM)[18-20]. In this method, 5 mL of $1 \times 10^{-3} \text{M}$ Li^+ was taken in a beaker and its potential was measured using lithium ion selective electrode. The potential was then slowly varied in small increments ($\sim 5 \text{ mV}$) by addition of standard lithium solution ($1 \times 10^{-2} \text{M}$). After every addition, the stabilized potential was recorded and corresponding increase in lithium concentration (Δa_A) was calculated. In the second set of experiments, potential of 5 mL of $1 \times 10^{-3} \text{M}$ Li^+ was varied in similar increments by addition of standard solution of impurity ion (a_B) prepared. Concentration of lithium ion throughout the impurity ion addition was adjusted to $1 \times 10^{-3} \text{M}$ by adding required amount of lithium solution of known concentration. From the increase in concentrations of lithium 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:

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

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

3.3 Interference Studies

Interference of presence of HMTA, Urea, NH_4^+ , Na^+ and K^+ , ions on the potential measurement of lithium standard solution using coated wire lithium ion selective electrode was investigated by adopting matched potential method. The potential of the solution containing constant initial concentration ($1 \times 10^{-3} \text{M}$) of primary ion i.e. Li^+ , was varied by about 30 mV in four to five increments either by adding lithium std. solution or impurity ion solution. The selectivity coefficient obtained from these studies is summarized in **Table 1**. The results clearly showed that the impurity ions studies have negligible interference in lithium measurement. Among the various ions studied, HMTA was found to have highest selectivity coefficient indicating interference at high concentrations.

Table 1. Selectivity coefficient of impurities using coated wire Lithium ISE.

S.No.	Impurity ion	Selectivity Coefficient
1	Urea	8.24×10^{-2}
2	NH_4^+	3.54×10^{-3}
3	HMTA	9.97×10^{-1}
4	Na^+	3.42×10^{-3}
5	K^+	3.48×10^{-3}

3.4 Response of Coated Wire Li-ISE

The response of lithium ion selective electrode in one month time was given in **Figure 4**. It was found that the response of the electrode was found to be working satisfactory. In addition response time is another important factor for any ion selective electrode. Thus, in the case of all electrodes, the average response time required for the electrodes to reach a potential response within $\pm 1 \text{ mV}$ of final equilibrium values after successive immersion in a series of solutions each having a 10-fold difference in concentration was measured. In this study, the practical response time was recorded by changing solutions with different low-to-high lithium concentration. As can be seen, in the concentration range, the electrode reaches equilibrium response within few minutes. The measurement sequence was from the lower ($1 \times 10^{-3} \text{M}$) to the higher ($1 \times 10^{-2} \text{M}$) concentration. Characteristic performance of coated wire lithium ion selective electrode was shown in **Table 2**.

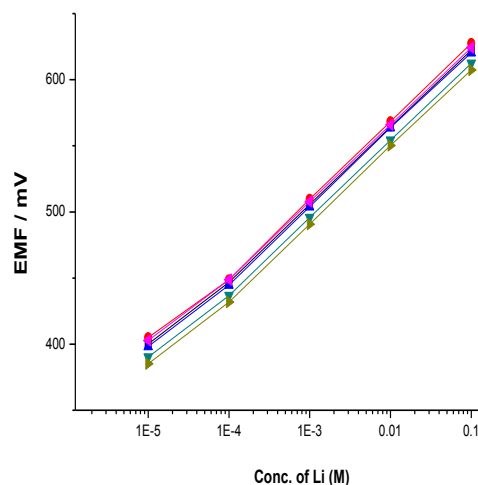


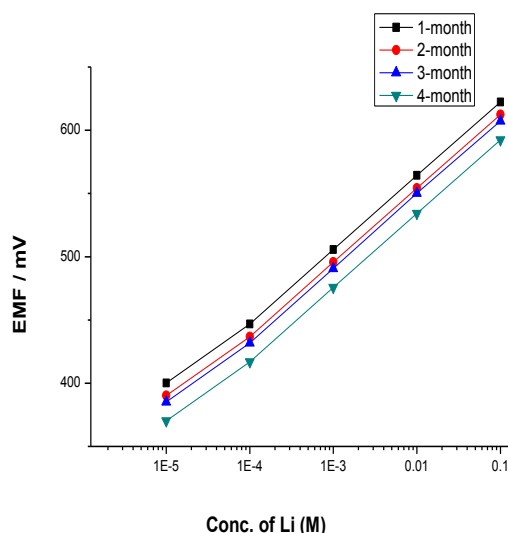
Figure 4 Response of Li ion selective electrode in one month since fabrication.

3.5 Life Time of Coated Wire Li-ISE

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

Table 2 Response characteristics of the coated wire lithium ion selective electrode.

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

**Figure 5** Lifetime of Li-ion selective electrode.

3.6 Analytical Applications of Coated WIRE Li-ISE

In order to ascertain that there is no significant interference in the determination of lithium due to the presence of organic matrix using coated lithium ion selective electrode, all the washing sample containing Li (natural) received from the preparation of Li₂TiO₃ microspheres were diluted prior to lithium analysis. It was observed that the concentration of Li in the mixture matched within 2% of the expected values which proved the absence of any significant interference owing to organic constituents. **Table 3** shows the data on the determination of lithium in synthetic mixtures containing organic components (HMTA, urea). The precision of the method was also ascertained by repetitive determination of Li in one of the samples and was found to be better than 0.5%.

Table 3 Determination of lithium in from solutions of synthetic mixture (containing HMTA+Urea) using coated wire lithium ion selective electrode

Sample	Coated Li ISE (*) (M)	Expected (B)	A/B
Li-Mix-1	1.541±0.031	1.53	1.007
Li-Mix-2	1.537±0.031	1.55	0.992
Li-Mix-3	1.554±0.031	1.54	1.009
Li-Mix-4	1.569±0.031	1.55	1.012
Average			1.005 ±0.020

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

3.7 Storage of Coated Wire Li-ISE

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

4. CONCLUSIONS

The results from the above experiments demonstrate the usefulness of the coated wire lithium ion selective electrode for the determination of lithium in complex chemical mixture containing various organic materials and solvent. These studies were found to be highly useful in the optimization of the washing conditions in sol-gel process for obtaining phase pure lithium titanate sol-gel particle. The methodology developed in this work is fast and precise and can be employed on a routine basis for lithium determination in solutions containing organic constituents.

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5. REFERENCES

- [1]. R. Y. Xie, G. D. Christian, (1986) Serum lithium analysis by coated wire lithium ion selective electrodes in a flow injection analysis dialysis system, *Analytical Chemistry*, **58(8)**,1807.
- [2]. J. H. Sim, K. M. Lee, J. S. Lee, D. H. Cho, H. Nam, G. S. Cha, (2001) Lithium ion-Selective electrode with improved lifetime, *Bulletin of Korean Chemical Society*, **22(7)**, 765.
- [3]. A. Okorodudu, R. W. Burnett, R. B. McComb, G. N. Bowers, Jr., (1990) Evaluation of three first-generation ion-selective electrode analyzers for lithium, *Clinical Chemistry*, **36(1)**, 104.
- [4]. Y. R. Kang, K. M. Lee, H. Nam, G.S. Cha, S. O. Jung, J. S. Kim, (1997) Lithium ion-selective electrodes employing tetrahydrofuran-based 16-Crown-4

- derivatives as neutral carriers, *Analyst*, **122**, 1445.
- [5]. V. P. Y. Gadzekpo, J. M. Hungerford, A. M. Kadry, Y. A. Ibrahim, G. D. Christian (1985) Lipophilic lithium ion carrier in a lithium ion selective electrode, *Analytical Chemistry*, **57**, 493.
- [6]. R. L. Bertholf, M. G. Savory, K. Winbome, J. C. Hundley, G. M. Plummer, J. Savory, (1988) Lithium determined in serum with an ion-selective electrode, *Clinical Chemistry*, **34(7)**, 1500.
- [7]. M. M. Jonas, F. E. Kelly, R. A. F. Linton, D. M. Band, T. K. O'Brien, N. W. F. Linton (1999) A comparison of lithium dilution cardiac output measurements made using central and antecubital venous injection of lithium chloride. *Journal of Clinical Monitoring & Computing*, **15**, 525-528.
- [8]. R. Govindan, D. Alamelu, V. Raju, Shah, T. V. Vittal Rao, Y. R. Bamankar, A. R. Parab, K. SasiBhushan, S. K. Mukerjee, S. K. Aggarwal (2010) Determination of lithium by potentiometry using fluoride ion selective Electrode, *Analytical Methods*, **2**, 1752-1755.
- [9]. V. N. Vaidya, S. K. Mukerjee, J. K. Joshi, R. V. Kamat, D. D. Sood, (1987) A study of chemical parameters of the internal gelation based sol-gel process for uranium dioxide, *Journal of Nuclear Materials*, **148**, 324-331.
- [10]. S. Suryanarayana, N. Kumar, Y. R. Bamankar, V. N. Vaidya, D. D. Sood (1996), Fabrication of UO₂ pellets by gel pelletization technique without addition of carbon as pore former, *Journal of Nuclear Materials*, **230**, 140.
- [11]. H. Hamilton (1995) The thermal cycling behavior of lithium titanate, *Journal of nuclear materials*, **219**, 274-283.
- [12]. C. E. Johnson, K. R. Kummerrer, E. Roth (1988) Ceramic breeder materials *Journal of Nuclear Materials*, **155-157**, 188-201.
- [13]. C. E. Johnson (1991) Research and development status of ceramic breeder materials, *Journal of Nuclear Materials*, **179-181**, 42-46.
- [14]. D. L. Smith (1984) Evaluation of candidate blanket materials for fusion reactor blanket applications, *Journal of Nuclear Materials*, **122**, 51-65.
- [15]. N. Roux, J. Avon, A. Florencig, J. Mougin, B. R. Asneur, S. Rabel (1995) Proc. 4th International workshop on ceramic breeder blanket interactions, p. 452
- [16]. T. V. Vittal Rao, Y. R. Bamankar, S. K. Mukerjee (2007) Proceedings of the XIV International sol-gel conference (ISGC), Montpellier, France, p. 210
- [17]. T. V. Vittal Rao, Y. R. Bamankar, S. K. Mukerjee, S. K. Aggarwal (2012) Preparation and characterization of Li₂TiO₃ pebbles by internal gelation sol-gel process, *Journal of Nuclear Materials*, **426**, 102-108.
- [18]. 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.
- [19]. V. P. Y. Gadzekpo, G. Christian, (1984) Determination of selectivity coefficients of ion selective electrodes by a matched-potential method, *Analytica Chimica Acta*, **164**, 279-282.
- [20]. Y. Umezawa, K. Umezawa, H. Sato, (1995) Selectivity coefficients for ion-selective electrodes-recommended methods for reporting $K_{A,B}^{pot}$ values, *Pure and Applied Chemistry*, **67** 507-518.

***Bibliographical Sketch**



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