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Article

Construction of a New Aluminum(III) Cation Selective Electrode Based on 12-Crown-4 as an Ionophore

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This article describes the fabrication of a novel and selective polyvinylchloride (PVC) membrane potentiometric sensor for Al^{3+} cation based on 12-crown-4 (12C4) as an ionophore. The electrode was prepared by coating the surface of a graphite rod by a membrane containing PVC as a plastic matrix, dibutylphthalate (DBP) as plasticizer, 12C4 as an ionophore and oleic acid (OA) as an additive. Under optimized membrane composition, the constructed electrochemical sensor exhibited a Nernstian response for Al^{3+} cation concentration, ranging from 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} with a detection limit of 5.5×10^{-7} mol L^{-1} and a slope of 19.0 ± 0.4 mV *per* decade at 25 °C. The constructed potentiometric sensor showed a relatively fast response time (15 s), good reproducibility and stability, and high selectivity towards Al^{3+} cation in solutions. The proposed sensor was successfully used as an indicator electrode in potentiometric titration and also in the direct determination of this metal cation in real samples.

Keywords: aluminum(III) cation, 12-crown-4, ion-selective electrode, potentiometry

Introduction

Today, aluminum with a high level in the earth's crust ranks third,[1] is the most widely used metal in the world after iron.[2] It is used in the manufacture of automobiles, packaging materials, electrical equipments, machinery, building construction and as a flocculating agent in potable water treatment units.[1] High levels of aluminum can interfere with the metabolism of phosphorus, resulting in a variety of bone lesions[3,4] and also it has been known that this element causes dementia, anemia, myopathy, bone and joint diseases.[3-5] Many studies have focused on the toxicity of aluminum on living systems especially on human beings and it is believed that aluminum plays important roles in the pathology of Parkinson's disease (PD), Alzheimer's disease (AD) and diseases of dialysis.[3,6-9] Therefore, the determination of aluminum in environment, medicine, foodstuff, etc., is very important.

Potentiometry is the most commonly used of the electrochemical techniques for determination of concentration of various analytes in solutions and it involves the measurement of potential (voltage) generated by an electrochemical cell under essentially equilibrium conditions.[10] Potentiometric ion-selective electrodes (ISEs) are one of the most important groups of chemical sensors. The application of ISEs has evolved to a well-established routine analytical technique in many fields, including clinical and environmental analysis, physiology, and process control.[11-13] The ion-selective electrodes are used for determination of particular species in aqueous, non-aqueous and mixed solvents and also the partial pressures of the dissolved gases in solutions.[14] An ion-selective electrode generates a difference in electrical potential between itself and a reference electrode and its output potential is proportional to the amount or concentration of a selected ion in solution.

The advantages of ISEs over many other chemical sensors, for cation and anion detections are their easy handling, non-destructive analysis, accuracy, reproducibility, wide working range, relatively fast response, sufficiently reliable and reasonable selectivity, and facility in construction and also inexpensive sample preparation. These electrodes are being used in clinical analysis and in routine control analysis of some ions and some biological species.[15-17] They can simply be produced with a very low cost and above all, they allow us to analyze the solution without pre-treatments.[15-17]

In the present paper, we report the construction of an ion-selective electrode based on 12-crown-4 (Scheme 1)

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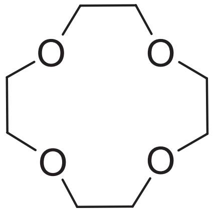
for determination of aluminum(III) cation in solutions. This ionophore has a good selectivity to Al^{3+} cation compared with some of the other metal ions present in solution.



Scheme 1. Structure of 12-crown-4.

Experimental

Chemicals

Tetrahydrofuran (THF), 12-crown-4 (12C4), dibutylphthalate (DBP), oleic acid, potassium nitrate, calcium nitrate, magnesium nitrate, cerium(III) nitrate, cobalt(II) nitrate, manganese(II) chloride, yttrium nitrate, ferric nitrate, and zinc(II) nitrate were purchased from Merck. Ethylene diamine tetraacetic acid disodium salt (EDTA) (BDH), sodium nitrate (BDH), copper(II) nitrate (BDH), cadmium(II) nitrate (Riedel), lead(II) nitrate (BDH), chromium(III) nitrate (BDH), nickel(II) nitrate (Riedel) and aluminum nitrate (Riedel) were used without further purification. Polyvinyl chloride (PVC) powder was purchased from Sigma-Aldrich. All metal ion solutions were prepared in doubly distilled water by diluting 0.1 mol L^{-1} stock solutions.

Apparatus and potential measurement

The potentials were measured with a PHM-632 (Metrohm, Switzerland) potentiometer equipped with an Ag/AgCl reference electrode. The accuracy of the potentiometer was ±0.01 mV. The pH data were recorded on a digital pH meter (Metrohm). The measurements were carried out at 25 °C with a cell type:

Ag/AgCl;KCl(sat.)//Al^{3+} sample solution/ion-selective electrode/graphite bar

The performance of the electrode was investigated by measuring the potential of Al^{3+} cation solutions over the range of 1.0×10^{-9} to 1.0×10^{-1} mol L^{-1} by serial dilution of the 0.1 mol L^{-1} stock solution. The solutions were stirred, and the potential was recorded when a steady state value was attained. Doubly distilled deionized water was used throughout.

Preparation of the electrode

The electrode was prepared from a graphite bar (3 mm diameter). The graphite bar was polished. A mixture of ionophore (12C4), PVC, plasticizer (DBP) and oleic acid (for increasing the electrical conduction and mechanical stability of coated membrane) to give a total mass of 100 mg was completely dissolved in about 2 cm^3 of THF in a glass beaker and the solution was mixed well. The solvent was evaporated slowly until an oily mixture was obtained and the graphite bar was dipped into the mixture for a few seconds. Next, the graphite bar was removed from the mixture, stored at room temperature for 24 h. Then, the coated electrode was conditioned in 0.01 mol L^{-1} aluminum nitrate solution for 24 h.

Results and Discussion

Complexation study of 12-crown-4 with aluminum(III) cation

In our preliminary studies to examine the interaction between Al(III) cation and the ligand, the complex formation between the ligand and aluminum(III) cation was investigated by electrical conductance method. The conductance measurements were performed using a digital JENWAY conductivity apparatus (model 4510) and in a water thermostat at a constant temperature, which was maintained within ±0.01 °C. The electrolytic conductance was measured using a cell consisting of two platinum electrodes, and an alternating potential was applied to the electrodes. In conductometric measurement, a solution of metal salt (1×10^{-4} mol L^{-1}) was placed in a titration cell at 25 °C, and the conductance of the solution was measured. Then a step-by-step increase of the crown ether solution prepared in the same solvent (2×10^{-3} mol L^{-1}) was carried out by a rapid transfer to the titration cell using a microburette and the conductance of the solution in the cell was measured after each transfer at 25 °C.

The change in molar conductivity (Λ_m) *versus* the ligand to cation molar ratio ($[L]_t/[M]_t$) was studied to determine the stability constant for the complexation of 12-crown-4 with aluminum(III) cation in acetonitrile (AN). The change in Λ_m *vs.* $[12C4]_t/[Al^{3+}]_t$ ratio is shown in Figure 1. As is evident from Figure 1, a relatively stable 1:1 complex is formed between the aluminum(III) cation and 12C4 in solution. In order to underline the validity of the 1:1 [ML] complexation model, the fitting and experimental curves for $(12C4.Al)^{3+}$ complex in pure AN solution at 25 °C are shown in Figure 2. As shown in this Figure, there is a very good agreement between the fitting and experimental data. Hence, our assumption of 1:1 stoichiometry for the complexation process seems reasonable. As is evident in Figure 1, addition of 12C4 to Al^{3+} cation solution in pure AN results in an increase in molar conductivity which indicates that the $(12C4.Al)^{3+}$ complex is more mobile than free solvated Al^{3+} cation. The stability constant (log K_f) of $(12C4.Al)^{3+}$ complex at 25 °C was calculated from the changes of the molar conductance as a function of ligand/cation mole ratios using a GENPLOT computer program[18] and it was found to be 3.36 ± 0.08. The details of the calculation of the stability constants of metal ion-complexes by conductometric method have been described elsewhere.[19] Thus, the obtained results clearly indicate that 12-crown-4 can act as a suitable ionophore for construction of Al^{3+} cation-selective electrode.

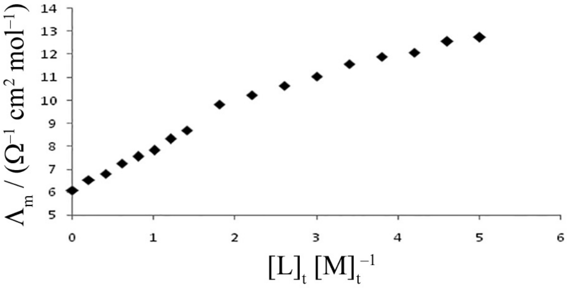


Figure 1. Molar conductance-mole ratio plots for $(12C4.Al)^{3+}$ complex in AN at 25 °C.

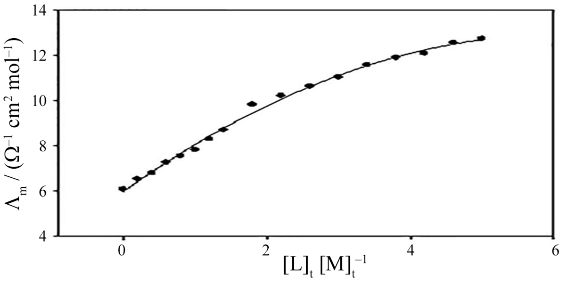


Figure 2. Fitting and experimental curves for $(12C4.Al)^{3+}$ complex in AN at 25 °C (● experimental curve, – fitting curve).

Components of ion-selective electrodes

Membrane composition has a great effect on the sensitivity, selectivity and stability of the ion-selective membrane electrodes.[20] The sensing layer of most ISEs is comprised of an organic polymeric membrane matrix.[21] Each of the components of the sensing layer is entrapped within a polymer membrane that subsequently is used to construct an electrode. The most widely employed polymer for construction of ISE membranes is PVC, a fact that can be attributed to its relatively cheap cost, good mechanical properties, and amenability to plasticization.[21] For PVC-based ISEs, typical weight ratios of polymer to plasticizer are approximately 1:2.[22-24] Additionally, since the membranes comprise a high percentage of plasticizer, this component acts as the solvent for all membrane constituents and, hence, should be compatible with these species. Aside from yielding desired physical properties of the membranes and acting as a solvent, studies have demonstrated that the nature of the plasticizer can have an effect on the performance of the ISE. The plasticizer is typically selected based on compatibility with the ionophore (solubility reasons) and the ultimate application of the ISE.[21]

The most important component of a membrane with respect to the selectivity of a chemical sensor, is the ionophore. Indeed, the event measured at the molecular level by the ISE is the binding between the ion of interest and the ionophore. The selectivity of an ISE can ultimately be attributed to the difference in binding strengths between various ions and the ionophore from which the sensor is constructed. The final component of an ion-selective membrane is normally an ionic additive that is sufficiently lipophilic to remain solely in the organic membrane phase when in contact with aqueous solution. Ionic additives are employed to ensure that the ISE membranes are permselective, that is, that either cations or anions are extracted into the membrane with no significant amounts of a counter ion being co-extracted.[25-27]

In the present work, PVC as a polymer matrix, DBP as plasticizer, 12C4 as an ionophore, oleic acid (OA) as additive and THF as a solvent were used for construction of the ion-selective electrode. The membranes for construction of the potentiometric sensor were prepared with different amounts of the crown ether, plasticizer (DBP), OA and PVC (Table 1). The composition of the PVC-membranes were optimized by varying the ratio of the ionophore, plasticizer, oleic acid and PVC to obtain the membranes showing the best performance regarding the working concentration range, slope and response time. The experimental results, which are summarized in Table 1, indicate that the membrane number 1 with the composition of DBP:PVC:OA:12C4 in the percentage ratio of 61.5:29:6.5:3 (m/m, mg) shows a Nernstian behavior for the proposed electrochemical sensor. The calibration curve obtained by this electrode is shown in Figure 3. The response of this membrane electrode of varying Al^{3+} concentration depicts a wide linear range from 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} with a Nernstian slope of 19.0 ± 0.4 mV *per* decade and a detection limit of 5.5×10^{-7} mol L^{-1}. The Nernstian slope for ion-selective electrodes must be 59.1/z mV *per* decade at 25 °C, therefore, we selected the membrane number 1 for construction of the electrode. The proposed electrode was very stable and could be used for two months without any change in its response characteristics.

Table 1. Optimization of membrane ingredients

	Membrane composition / mg						
Membrane No.	PVC / wt.%	Plasticizer (DBP) / wt.%	12C4 / wt.%	Additive (OA) / wt.%	Slope / (mV *per* decade)	R^2	Linear range / (mol L^{-1})
1	29	61.5	3	6.5	19.00	0.9950	10^{-1}-10^{-6}
2	29	62	6.5	2.5	26.32	0.9941	10^{-1}-10^{-6}
3	29	61.5	2.5	7	34.00	0.9944	10^{-1}-10^{-6}
4	29	62	3	6	21.00	0.9643	10^{-1}-10^{-6}
5	29	64	3	4	20.60	0.9845	10^{-1}-10^{-6}
6	28	64	4	4	21.14	0.9795	10^{-1}-10^{-6}
7	28	63	3	6	18.81	0.9573	10^{-1}-10^{-6}
8	29	60	3.5	7.5	17.88	0.9783	10^{-1}-10^{-6}
9	28	61	3.5	7.5	16.25	0.9856	10^{-2}-10^{-6}
10	28	62	3	7	20.88	0.9911	10^{-1}-10^{-6}
11	28	62	3.5	6.5	18.32	0.9764	10^{-1}-10^{-6}
12	27	63	4	6	25.15	0.9848	10^{-1}-10^{-4}
13	27	62	3.5	7.5	17.35	0.9712	10^{-2}-10^{-6}
14	30	64	3	3	25.04	0.9726	10^{-1}-10^{-5}
15	31	63	3	3	–	–	–

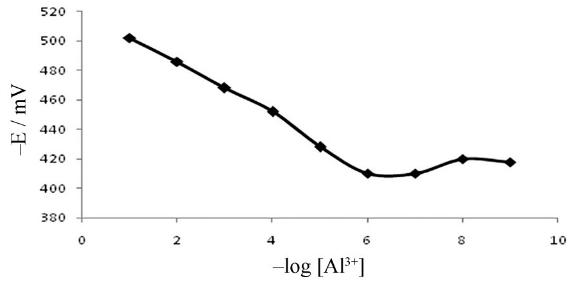


Figure 3. Calibration curve of Al^{3+}-selective electrode based on 12C4.

Effect of pH

The relationship between the pH and the potentials of the ion-selective electrode was investigated by measuring the potential at two Al^{3+} concentrations (1.0×10^{-3} and 1.0×10^{-4} mol L^{-1}) at a pH range 1-12, where the pH was adjusted with HNO_3 or NaOH. The effect of the pH on the potential response of the electrode is shown in Figure 4. As is shown in this Figure, the potential remains constant over a pH range of 4.0-8.0. Therefore, the working pH range of the proposed electrode is 4.0-8.0. A significant change in the potential response is observed at pH greater than 8.0, which may be due to the formation of hydroxyl complexes of Al(III) cation, in solution. At low pH values, the potential increases, which indicates that the membrane sensor responded to hydrogen ions in solution. In the subsequent measurements, we adjusted the pH of the solutions to 5 by using acetic acid/sodium acetate buffer solution.

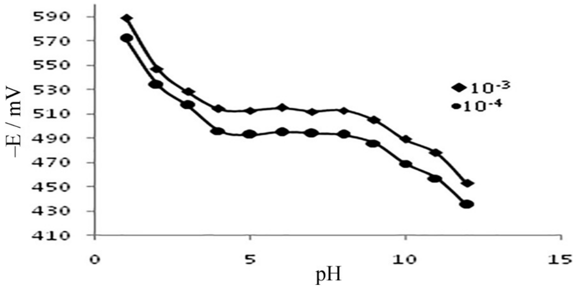


Figure 4. Effect of pH on potential response of the Al^{3+}-selective membrane electrode using (◆) 1.0×10^{-3} mol L^{-1} and (●) 1.0×10^{-4} mol L^{-1} of Al^{3+} solutions.

Static and dynamic response times and reversibility of the electrode

The response time is one of the most important factors for analytical applications of ion-selective electrodes. In order to evaluate the practical static response time of the electrode, the average time required to achieve a potential within ±1 mV of the final steady state potential was measured by recording the potential-time plots for three different concentrations of Al^{3+} cation and the results are shown in Figure 5. The results clearly show that, in all cases, the electrode demonstrates a constant and stable potential within 15 s. Furthermore, the practical dynamic response time of the electrode was recorded by changing the concentration of Al^{3+} cation in solution. The measurement sequence was from the lower (1.0×10^{-6} mol L^{-1}) to the higher (1.0×10^{-1} mol L^{-1}) concentrations and the results are shown in Figure 6. In order to evaluate the reversibility of the proposed electrode, a similar procedure was performed in the sequence of 1.0 × 10^{-3} and 1.0 × 10^{-4} mol L^{-1} Al^{3+} cation concentrations for 3 times, and the graphical results are shown in Figure 7. As is evident from this Figure, the potentiometric response of the sensor is quite reversible when it was consecutively dipped in two solutions alternatively for 3 times.

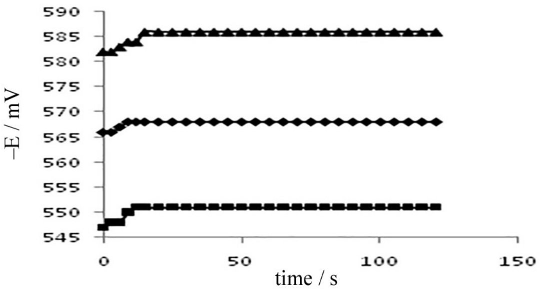


Figure 5. Static potential-time plots for three different Al^{3+} concentrations: (▪) 1.0 × 10^{-2} mol L^{-1}, (♦) 1.0 × 10^{-3} mol L^{-1}, (▲) 1.0 × 10^{-4} mol L^{-1}.

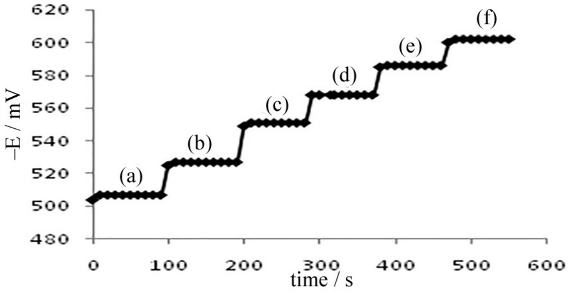


Figure 6. Dynamic response time of the Al^{3+} electrochemical sensor with step changes in the Al^{3+} concentration: (a) 1.0 × 10^{-6} mol L^{-1}, (b) 1.0 × 10^{-5} mol L^{-1}, (c) 1.0 × 10^{-4} mol L^{-1}, (d) 1.0 × 10^{-3} mol L^{-1}, (e) 1.0 × 10^{-2} mol L^{-1}, (f) 1.0 × 10^{-1} mol L^{-1}.

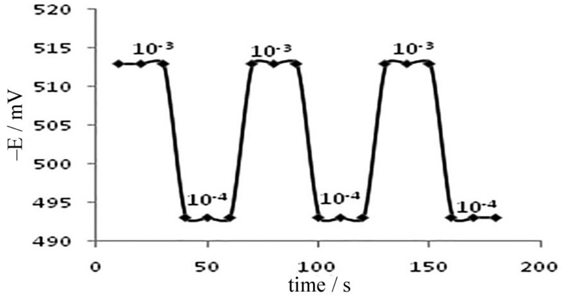


Figure 7. Response characteristics of the Al^{3+}-selective membrane electrode for several high-to-low (1.0 ×10^{-3} to 1.0 ×10^{-4} mol L^{-1}) sample cycles.

Evaluation of selectivity coefficients

The selectivity behavior is obviously one of the most important characteristics of an ion-selective electrode, determining whether a reliable measurement of a target analyte in a sample solution is possible.[21,28] The influence of interfering ions on the response behavior of ion-selective membrane electrodes is usually described in terms of selectivity coefficients ($K^{Pot}_{Al,M}$). In the present work, for determination of the selectivity, the separated solution method (SSM) was applied.[29,30] In SSM, the potential of a cell comprising an ion-selective electrode and a reference electrode is measured with two separate solutions, one containing the ion A at the activity a_A (but no B) and the other one containing the ion B at the same activity $a_A = a_B$ (but no A).[31] If $K^{Pot}_{A,B}$ is bigger than 1, the ISE responds to the interfering ions more selectively than to the analyte ions. In most cases, $K^{Pot}_{A,B}$ is smaller than 1, which means that such ISEs respond to the primary ion more selectively than to the interfering ions.[31] The values of the selectivity coefficients for various metal cations, which are summarized in Table 2, clearly indicates that the electrode is selective to Al^{3+} cation over a number of the other metal cations present in solutions. In the case of interference of the Ce^{3+} and Cr^{3+} cations, as evident in Table 2, the selectivity coefficient $K^{Pot}_{Al,M}$ is less than one even when their concentrations are 1000 times higher than Al^{3+} cation in solution.

Table 2. Values of selectivity coefficients for different ionic interferences (M^{n+}) for Al^{3+}-ISE

M^{n+}	$K^{Pot}_{Al,M}$
K^+	5.38 × 10^{-7}
Na^+	1.38 × 10^{-8}
Ca^{2+}	3.13 × 10^{-8}
Mg^{2+}	1.90 × 10^{-9}
Co^{2+}	1.19 × 10^{-9}
Mn^{2+}	2.32 × 10^{-10}
Zn^{2+}	1.55 × 10^{-8}
Ni^{2+}	5.69 × 10^{-4}
Cd^{2+}	3.64 × 10^{-7}
Cu^{2+}	7.32 × 10^{-7}
Pb^{2+}	8.32 × 10^{-7}
Cr^{3+}	0.44
Ce^{3+}	0.14
Fe^{3+}	7.19 × 10^{-4}
Y^{3+}	7.71 × 10^{-9}

Applications

Potentiometric titration

The proposed membrane electrode for Al^{3+} ion was found to work well under laboratory conditions. The electrode was used as an indicator electrode in the successful titration of 25 cm^3 of Al^{3+} cation (1.0 × 10^{-3} mol L^{-1}) with an EDTA solution (1.0 × 10^{-2} mol L^{-1}) at pH 5, where the pH was adjusted with acetic acid/sodium acetate buffer solution. Doubly distilled deionized water was used to prepare the solutions. The resulting titration curve and the corresponding d*E* d*V*$^{-1}$ *vs.* volume graph for the titration of Al^{3+} cation solution with EDTA are shown in Figures 8 and 9, respectively. These graphical results show that the amount of Al^{3+} cation can be accurately determined with the ion-selective electrode.

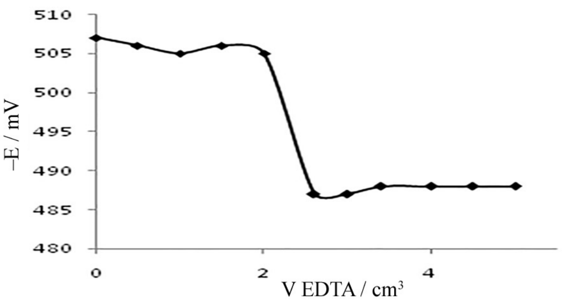


Figure 8. Potentiometric titration curve of 25 cm^3 of 1.0×10^{-3} mol L^{-1} Al^{3+} cation with 1.0×10^{-2} mol L^{-1} of EDTA, using the proposed electrode.

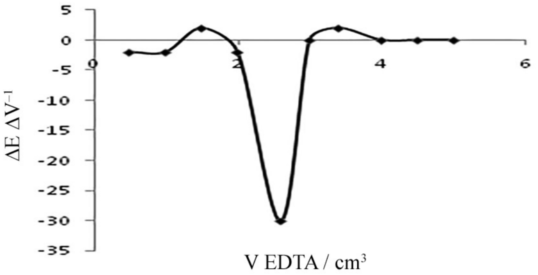


Figure 9. Differential potentiometric titration curve of 25 cm^3 of 1.0×10^{-3} mol L^{-1} Al^{3+} with 1.0×10^{-2} mol L^{-1} of EDTA, using the proposed electrode.

Determination of Al^{3+} in real samples

A crushed sample of 0.2 g of some rocks (e.g., andesite, basalt, granite, rhyolite) was dissolved in 10 cm^3 of 20 mol L^{-1} HF solution under gentle heating condition and the heating was continued up to about dryness of the samples. The reminder was dissolved in 5 cm^3 of 4 mol L^{-1} H_2SO_4 and diluted to 25 cm^3 with doubly distilled water and each of the solutions were diluted 250 times. Then, acetic acid/sodium acetate buffer solution was added for pH adjustment at 5. Finally, the solutions were titrated by a standard solution of EDTA.

In addition, the proposed electrode was applied for determination of aluminum in aluminum-magnesium syrup (prepared from Alborz Darou). For the preparation of sample, 1 cm^3 of Al-Mg syrup was heated in a furnace to dryness. The remainder was dissolved in nitric acid and diluted to 50 cm^3. The aluminum(III) cation concentration in the real samples was determined using the electrode by the calibration plot method. The concentration of aluminum in the rock samples and aluminum-magnesium syrup was also determined by flame atomic emission spectrometry (AES). In addition of titration Al^{3+} cation by EDTA, we have also used direct potentiometric method using the calibration plot ($y = -19.11x + 615$, $R^2 = 0.995$). The results obtained for real samples are summarized in Table 3. As is evident in this Table, there is a very good agreement between the experimental results obtained from potentiometric titration of Al^{3+} cation using the ion-selective electrode and atomic emission spectrometry.

Conclusions

The constructed new aluminum(III) electrochemical sensor incorporating 12-crown-4 can be used to for determination of Al^{3+} cation in solutions. Under optimized membrane composition, the electrochemical sensor exhibited a Nernstian response for Al^{3+} cation concentration, ranging from 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} with a detection limit of 5.5×10^{-7} mol L^{-1} and a slope of 19.0 ± 0.4 mV *per* decade at 25 °C. The proposed electrode was very stable and could be used for two months without any change in its response characteristics. The inherent advantages of the proposed electrodes are its simple operation, high selectivity and sensitivity, good stability and reproducibility, low cost and a wide linear range, low detection limit and fast

Table 3. Potentiometric determination of aluminum(III) in real samples using Al^{3+} cation-selective membrane sensor based on 12C4 and atomic emission spectrometry

Real sample	Al^{3+} content		
	AES / ppm	Direct potentiometric / ppm	Potentiometric titration with EDTA by ISE / ppm
Andesite	3.980 ± 0.005	4.09 ± 0.10	4.32 ± 0.08
Basalt	3.69 ± 0.08	3.62 ± 0.09	3.78 ± 0.05
Rhyolite	4.98 ± 0.24	4.61 ± 0.16	4.86 ± 0.21
Granite	3.07 ± 0.23	3.21 ± 0.18	3.24 ± 0.19
Al-Mg syrup	2.85 ± 0.29	2.84 ± 0.20	3.00 ± 0.25

response time (15 s). Meanwhile, the proposed sensor can be successfully applied for determination of Al^{3+} cation in real samples and as an indicator electrode in potentiometric titration of Al^{3+} ion with EDTA.

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