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Developing Potentiometric PVC-Plasticized Sensors for Sc^{3+} †

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Abstract: Nowadays scandium is widely used in high-tech fields such as electronics, aerospace, optics, catalysis, and metallurgical industries due to its unique physical, chemical, electric and magnetic characteristics. With the growth of miscellaneous commercial applications of this element and its compounds, monitoring of scandium in technological processes is in demand and thereby making it interesting in the analytical chemistry area. Different conventional analytical methods have been employed to measure scandium, and the most often applied are ICP-MS and ICP-AES. Despite the high precision and sensitivity of these tools, serious drawbacks including sophisticated and time-consuming analysis limit their wide use. On the other hand, potentiometric sensors possess merits over these conventional analytical methods due to their cost-effectiveness and reagent-free procedures as well as their reasonable precision and rapid response time. Potentiometric sensors based on polymeric membranes are routinely used to measure different cations and anions, but no study has yet been carried out for scandium sensors. This research is devoted to the development of Sc^{3+} potentiometric sensors. A series of potentiometric electrodes with polymer plasticized membranes was prepared using different neutral ligands adopted from liquid extraction of rare earth metals as sensing components. These ligands include phosphine oxides and diamides of various organic acids. The membranes also contained poly(vinylchloride) as polymeric matrix, o-nitrophenyloctyl ether as a solvent-plasticizer, and chlorinated cobalt dicarbollide or fluorinated tetraphenyl borate derivatives as cation-exchangers. Sensors exhibited Nernstian or super-Nernstian response towards Sc^{3+} across the concentration range (10^{-5} – 10^{-3} M) with a low detection limit of about 0.4 mg/l in acidic media (pH = 2). Interferences from other rare earth metals were measured by the separate solution method, and most of the proposed sensors were found to be more selective towards Sc^{3+}. Reproducible, stable, and precise results for sensing properties of the developed sensors imply the relevance of using these instruments for scandium quantification in real technological solutions.

Keywords: potentiometric sensors; ion-selective electrodes; scandium measurement; neutral ionophores; rare earth metals

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1. Introduction

Ekaboron, with the atomic number of 21, was first predicted by Dmitry Ivanovich Mendeleev in 1869 by observing a gap of atomic weight between Calcium and Titanium. It was renamed to Scandium after being discovered in Scandinavia Peninsula in 1879 by Lars Fredrik Nilsson, the Swedish chemist, through studying euxenite and gadolinite ores in Uppsala [1]. Scandium has an intermediate position between lanthanides and light metallic elements in the periodic table of elements [2] and has similar chemical properties to lanthanides. It is found as Scandia Sc_2O_3 in different ores such as thortveitite $Sc_2Si_2O_7$, sterrettite ($ScPO_4.2H_2O$), euxenite, gadolinite, and bazzite ($Be_3Sc_2Si_6O_{18}$). These ores generally contain trace amounts (0.005–0.3 wt.%) of Scandium. Nowadays, scandium is produced as a by-product of ores residues in the production of other metals such as uranium, titanium, tungsten, etc [3,4]. The methods employed to extract scandium from these residues include precipitation, solvent extraction, solid-phase extraction, cloud phase extraction, ion exchange, floatation, fractional crystallization, etc [2–4].

Despite being expensive, due to its scarcity, commercial applications of scandium are growing in high technology fields such as optic, electronic, aerospace, catalysis, fuel cells, as well as nuclear medicine [3,4]. Furthermore, it is widely used in metallurgical industry, in particular, manufacturing aluminium-scandium alloys due to its unique electric, physical, and chemical features [2,3,5]

Mining activities and industrial wastes are major sources of scandium release into the environment. Besides, infiltration of rainfall water into the soil near abandoned mining sites and tailings can lead to dissolution of scandium and other metals, and consequently, contaminate ground and underground water and soil. Similarly, it is capable of bioaccumulating in plants and making effect on the growth of algae [4]. Thus, both the growing applications of scandium and its environmental effects emphasize the importance of developing accurate methods for measuring this element

Currently, the most universal methods for the quantitative determination of scandium are inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) techniques which exhibit high sensitivity to the Sc^{3+} ion and provide reproducible and precise results as well as a relatively wide measurement range. However, their use is limited due to serious disadvantages such as high equipment and operating costs, need for trained staff, time-consuming sample preparation steps, matrix effect, and presence of the spectral interferences due to the isotropic nature of scandium [6–8]. Neutron activation analysis (NAA) method has the same drawbacks as the aforementioned methods. Besides, the intervals during measurement are long, and usually last about three weeks [9]. The XRF method has lower sensitivity compared to other methods; therefore, using this method for determining lower concentrations is burdened with significant error.

On the other hand, potentiometric sensors can be considered as an appropriate alternative to conventional analytical methods since they have major advantages over these techniques like high sensitivity, reproducibility, low detection limit, rapid response time, and cost-effectiveness. Furthermore, not only can these systems be used for real-time measurement, but also they are capable of being miniaturized [10,11]. Plasticized PVC is the most popular type of membrane matrix for ion-selective electrodes, and many ionophores and membrane compositions are applied for the environmental monitoring of different analytes. Developing potentiometric sensors for scandium detection would be a challenging task because of high hydrophilicity and similar chemical properties to lanthanides [12].

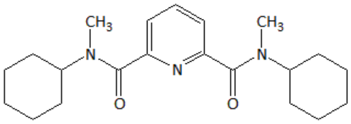
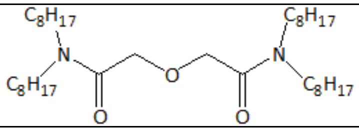
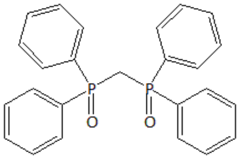
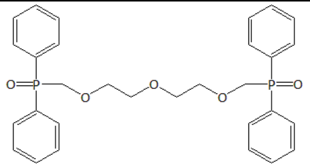
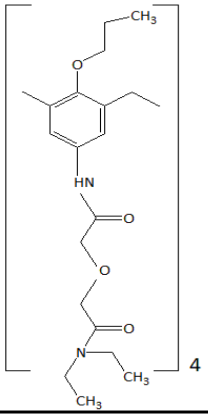
The aim of the present study is the development of potentiometric sensors for the detection of scandium. Noteworthy, no study has yet been performed for scandium detection by potentiometric sensors.

2. Experimental

2.1. Reagents and Chemicals

The polymeric membrane matrix of electrodes was composed of poly(vinyl chloride) (PVC) (33 wt.%) as a polymeric matrix and 2 - nitrophenyloctyl ether (NPOE) as a plasticizer (59.5–64.3 wt.%). 10 mmol/kg sodium tetrakis[3,5-bis(trifluorometyl)phenyl]borate (NaTFPB) or the acidic form of chlorinated cobalt dicarbollide (CCD) were used as cation-exchangers (0.89 wt.% and 0.53 wt.%, respectively). PVC, NPOE, and NaTFPB were obtained from Merck (Darmstadt, Germany) in Selectophore® grade. CCD was provided by Katchem (Prague, Czech Republic). All sensor membranes contained 50 mmol/kg of one of the ligands listed in Table 1. ligands were selected based on liquid extraction literature data [12]. These ligands contain phosphine oxides, ether, and diamide functional groups and were purchased from Sorbent Technologies, LLC (Moscow, Russia). Tetrahydrofuran (THF) as a solvent was purchased from Merck and used as received. Nitrate salts of metals were purchased from Sigma-Aldrich (Germany), and were used without further purification. Doubly distilled water was used for solutions preparation.

Table 1. Description of the studied ligands.

Sensor	Composition	Chemical structure
M1	N,N′-Dimethyl-N,N′-dicyclohexyldiamide of dipicolinic acid	
M2	N,N,N',N'-Tetraoctyldiglycolamide (TODGA)	
M3	Tetraphenylmethylene diphosphine dioxide	
M4	1,9-Bis-(diphenylphosphynyl)-2,5,8-trioxanonane	
M5	5,11,17,23-Tetra(diethylcarbamoyl-ethoxymethylcarboxamido)-25,26,27,28-tetrapropoxycalix[4]aren	

2.2. Sensors Preparation

The sensor membranes were prepared using a standard protocol. The weighted amounts of membrane components were dissolved in freshly distilled THF and poured into flat bottomed Teflon beakers, and were left overnight for solvent evaporation. Circular pieces (3 mm in diameter) were cut from the parent membrane of each composition and glued upon the end of PVC sensor bodies (4 mm outer diameter, 2.5 mm inner diameter, 90 mm long). These tubes were then equipped with inner Ag/AgCl electrodes, and were filled in with 0.01 M NaCl solution and then immersed in the same solution for 48 h before measurements to equilibrate sensor membranes with aqueous solutions.

2.3. Potentiometric Measurements

Following galvanic cell was used during experimental studies:

Cu|Ag|AgCl, KClsat|sample solution|membrane|NaCl, 0.01M|AgCl|Ag|Cu

The potential values of sensors were measured with 0.1 mV precision against the standard reference electrode using a multi-channel digital high-impedance millivoltmeter connected to a PC for data acquisition. Measurement time was 3 minutes for each sample solution. After each measurement sensors were washed with several portions of distilled water until initial readings in water was observed. Each sample solution was 50 ml. Solutions were magnetically stirred to eliminate mass transport resistance and reduce response time of the sensors.

2.4. Sensors characteristics

Calibration of the sensors was carried out in solutions containing 10^{-7} and 10^{-3} M of scandium metal ions at pH 2 (by nitric acid) to suppress hydrolysis. Sensitivity value of sensors were calculated as the slopes of the linear parts of the calibration curves and were averaged over at least three measurements. The potentiometric selectivity coefficients of the Sc^{3+} sensors were evaluated according to the separated solution method (SSM). Lower detection limit values of sensors were determined according to The potentiometric selectivity coefficients of the Sc^{3+} sensors were evaluated according to the separated solution method (SSM)/ bi-ionic potentials method (BIP) the standard procedure from the calibration measurements by finding the intersection between two linear segments of each calibration curve of scandium.

3. Results and discussion

The scandium response curve (the dependence between the potential of the sensors and the logarithm of the concentration) of the studied sensors is illustrated in Figure 1. All sensors showed a linear response at the concentration range of 10^{-5} to 10^{-3} M. Sensitivity values of sensors M1 to M5 were 27, 18, 22, 30, and 19 mV/dec respectively.

Sensor responses were stable and reproducible, and standard deviations of the reported values were not exceeded 2 $^{\mathrm{mV}}/_{\mathrm{pMe}}$, towards Scandium. According to Figure 2 it can be noticed that sensors showed pronounced sensitivity for scandium. The highest sensitivity to scandium was observed for sensors M1 and M4, similar to divalent cations. This super-Nernstian sensitivity is probably attributed to the existence of $Sc(NO_3)^{2+}$ ions in the solution. In the presence of neutral ionophores, triply-charged cations can bind nitrate anion and form $Sc(NO_3)^{2+}$. This complex shows the potentiometric response similar to doubly-charged ions.

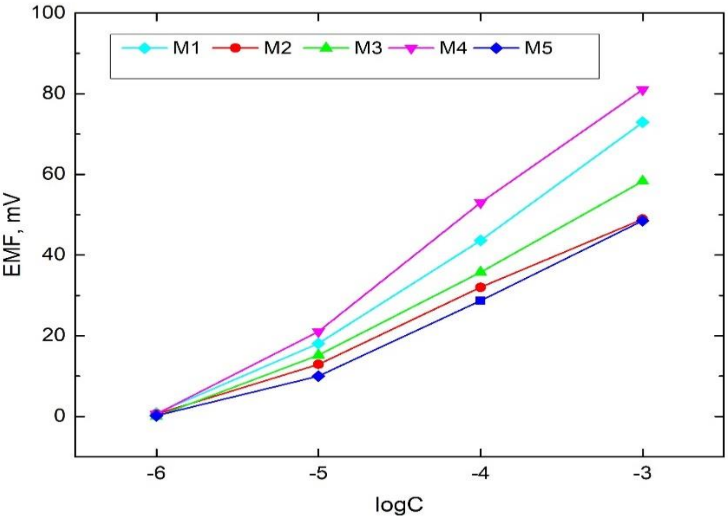


Figure 1. Potentiometric response curve for scandium at pH = 2.

The results of selectivity (in the term of the logarithm of the selectivity coefficient) of sensors for scandium towards lanthanides were calculated (Table 2). All data are averaged over three replicate measurements. Most of the sensors exhibited the good selectivity to scandium, because of negative values of $logk_{IJ}^{pot}$. The highest selectivity towards scandium was observed by the sensor M3 and M4 with ligands containing phosphine oxide functional groups.

Table 2. Selectivity coefficient values of the sensors towards scandium, $\pm 0.2 logK_{Sc,Me}^{pot}$.

Sensors	**La^{3+}**	**Eu^{3+}**	**Gd^{3+}**	**Lu^{3+}**
M1	−2.0	−2.2	−0.9	−1.3
M2	−2.3	−2.7	−0.2	−0.1
M3	−2.3	−3.0	−2.1	−2.8
M4	−1.3	−1.9	−1.3	−1.9
M5	−1.1	−0.1	+0.6	−0.3

Detection limits (LOD) of the sensors for scandium detection were calculated and the averaged values over three replicas for sensors M1 to M5 were 5.4, 5.8, 5.0, 5.1, and 5.5 in terms of are $pC_{Sc^{3+}}$ (SD<0.2) The dynamic response of sensor M5 is shown in Figure 2. As it is seen, the sensor reaches its steady response in a short time of about 30 s.

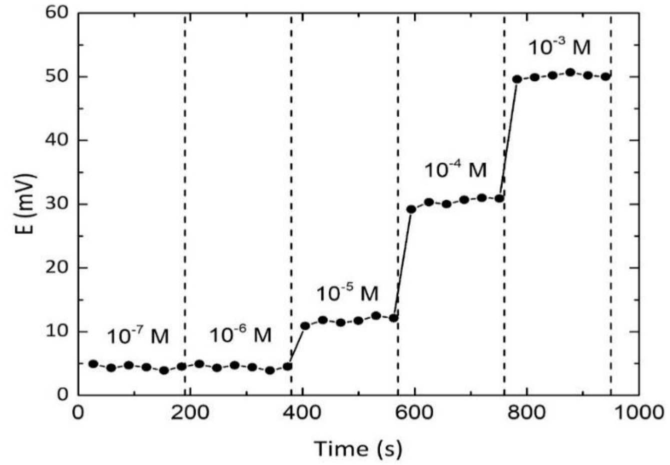


Figure 2. Dynamic response curve of the sensor M5 for step changes in scandium concentration.

4. Conclusion

In this study, potentiometric sensors based on PVC-plasticized membranes for detection of scandium were fabricated on the basis of extractive ligands in liquid extraction of lanthanides and actinides, and their electrochemical properties for detection of scandium were studied. Sensors exhibited pronounced sensitivity and good selectivity to scandium at $pH = 2$ with fast response time and low detection limit. Altogether, taking into account the cost and simplicity of the electrochemical sensors, the obtained outcomes exhibited a good potential for the development of new sensing devices alternative to the conventional analytical methods for scandium measurement.

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Conflicts of Interest: The authors declare no conflict of interest.

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