J. Braz. Chem. Soc., Vol. 18, No. 1, 215-222, 2007.
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0103 - 5053 $6.00+0.00

Article

Fabrication of a New Samarium(III) Ion-Selective Electrode Based on 3-{[2-Oxo-1(2*H*)-acenaphthylenyliden]amino}-2-thioxo-1,3-thiazolidin-4-one

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Este trabalho apresenta o desenvolvimento de um eletrôdo de membrana de PVC, que contém 3-{[2-oxo-1(2H)-acenonaftilideno]amino}-2-tioxido-1,3-tiazolidino-4-ona (ATTO), que mostrou ser seletivo para íons Sm^{3+}. Os dados obtidos mostram uma resposta Nernsteniana com inclinação de 19,3 ± 0,6 mV por década para íons Sm^{3+} em uma ampla faixa de concentração , de $1,0 \times 10^{-6}$ a $1,0 \times 10^{-1}$ mol L^{-1}. O limite de detecção encontrado foi $(5,5\pm 0.3) \times 10^{-7}$ mol L^{-1} numa faixa de pH entre 3,5 e 7,5, com tempo de resposta pequeno (~10 s). O sensor potenciométrico mostrou boa seletividade para diferentes cátions, como os alcalinos, alcalinos terrosos e para íons de metais pesados.

This paper introduces the development of an original PVC membrane electrode, based on 3-{[2-oxo-1(2*H*)-acenaphthylenyliden]amino}-2-thioxo-1,3-thiazolidin-4-one (ATTO) which has revealed to be a suitable carrier for Sm^{3+} ions. The resulting data illustrated that the electrode shows a Nernstian slope of 19.3 ± 0.6 mV *per* decade for Sm^{3+} ions over a broad working concentration range of 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1}. The lower detection limit was found to be equal to $(5.5\pm 0.3) \times 10^{-7}$ mol L^{-1} in the pH range of 3.5–7.5, and the response time was very short (~10 s). The potentiometric sensor displayed good selectivities for a number of cations such as alkali, alkaline earth, transition and heavy metal ions.

Keywords: PVC membrane, potentiometry, 3-{[2-oxo-1(2*H*)-acenaphthylenyliden]amino}-2-thioxo-1,3-thiazolidin-4-one, samarium(III) ion-selective electrode

Introduction

The increasing use of ion sensors in the fields of environmental, agricultural and medicinal analysis is stimulating analytical chemists to develop new sensors for fast, accurate, reproducible and selective determination of various species. In the past few decades, considerable efforts have led to the development of selective sensors for alkali, alkaline earth and heavy metals.[1]

Rare-earth oxides have numerous applications. For instance, they are used in the production of optical glasses, the preparation of glass fibers for optical purposes, gasoline-cracking catalysts, polishing compounds, carbon arcs. They are also used in iron and steel industries to remove sulfur, carbon and other electronegative elements from iron and steel.[2]

The determination of rare-earth ions is considered necessary, due to the growing interest in bioorganic and inorganic chemistry, various industrial applications of these species, and also their toxic and other adverse effects.

Rare earth species such as lanthanum ions accelerate hydrolysis of phosphate-ester binding by 13 orders of magnitude. This suggests that this compound can cause the same effect to the di-ester, in DNA. Lanthanum chloride manifests anti-tumor effects. Geno-toxicity of lanthanum(III) in human peripheral blood lymphocytes has also been reported. Lanthanum chloride has been reported to cause changes in lipid peroxidation, redox systems, and ATPase activities in plasma membranes of rice seeding roots.[3-5]

The first objective of the investigators was to classify the rare earths in accordance with the low acute toxicity rating. All the same, the toxicity of various erbium compounds showed that when inhaled, taken orally, or injected into the blood stream, erbium salts can cause serious problems.[6] Consequently, the detection of low concentrations of this ion in environmental solutions such as seawater is of great interest.[7]

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The available methods for the low-level determination of rare-earth ions in solution include MS spectrophotometry,[8] ICP-MS and ICP-AES,[9,10] isotope dilution mass spectrometry,[11] neutron activation analysis[12] and X-ray fluorescence spectrometry[13] are also used.

Samarium is a rare earth metal, with a bright silver luster. It is the first lanthanide reasonably stable in the air, but even so, it begins to show signs of oxidation after a few weeks. Natural samarium is a mixture of several isotopes, three of which are unstable due to short half-lives. Some applications of this element are in carbon-arc lighting in the motion picture industry (together with other rare earth metals), doping CaF_2 crystals for use in optical masers or lasers, as a neutron absorber in nuclear reactors, for alloys and headphones and samarium-cobalt magnets. Samarium oxide is a catalyst for the dehydration and dehydrogenation of ethanol, and is used in optical glass to absorb infrared light. Furthermore, samarium compounds act as sensitizers for phosphors exposed to infrared. Samarium is very dangerous in the working environment, due to the fact that damps and gasses can be inhaled with air. This can cause lung embolisms, especially during long-term exposures. Samarium can be a threat to the liver when it accumulates in the human body. Ion-exchange and solvent extraction techniques have recently simplified the separation of the rare earths from one another. More recently, electrochemical deposition using an electrolytic solution of lithium citrate and a mercury electrode has been claimed to be a simple, fast, and highly specific way to separate the rare earths.[14,15]

Following a literature survey, it was found that the most of the spectroscopic studies on the detection of samarium are carried out through inductively coupled plasma with or without mass spectrometry. Spectrophotometric study of the complexation of Sm ions, resonance ionization mass spectrometry, enhanced fluorimetric determination, studies on monoxide emission spectrometry, graphite furnace atomic absorption spectrometry, fluorescence and luminescent determination and fluorimetric methods and other methods like thermal ionization mass spectroscopy are also available.[16-19]

In addition, potentiometry with ion selective electrode has also been applied, for the same purpose since it presents the advantages of simplicity, high detection speed, and low cost.[20-25] In this study a new ion selective sensor to determine Sm^{3+} is introduced.

Several highly selective and sensitive membrane sensors for alkaline earth and transition metal ions have been reported.[26-35] In this study the development of a new ion selective sensor to Sm^{3+} determination and, in particular, the use of 3-{[2-oxo-1(2*H*)-acenaphthylenyliden]amino}-2-thioxo-1,3-thiazolidin-4-one (ATTO) as an excellent ionophore for the preparation of a highly Sm(III) ion-selective electrode (Figure 1) is reported.

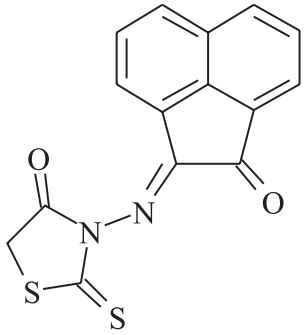

Figure 1. Structure of ATTO.

Experimental

Reagents

Merck and the Aldrich were the suppliers of nitrate and chloride salts of all cations, reagent grades of dibutyl phthalate (DBP), benzyl acetate (BA), 2-nitrophenyl octyl ether (NPOE), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and relatively high molecular weight PVC used in the experiments. All reagents were used without any further treatment. The nitrate and chloride salts of all employed cations were of the highest available purity and were only dried over P_2O_5 in vacuum. During all experiments, triply distilled deionized water was used.

ATTO synthesis

A mixture of acenaphthenequinone (0.01 mol, 1.82 g), 3-amino-2-thioxo-4-thiazolidinone (0.01 mol, 1.48 g) and a catalytic amount of acetic acid was refluxed in absolute ethanol (20 mL) for 3 h. After cooling to the room temperature, the red precipitate formed, was filtered, washed with ethanol (3 × 10 mL), and dried at 50 ºC, mp 290 ºC (decomposition), 2.9 g, yield 93%; IR (KBr) ν_{max}/cm^{-1}: 1741, 1705, 1687, 1602, 1473, 1315, 1229, 1109, 987, 895, 809; MS, *m/z* (%): 312 (M^+, 27). Anal. Calc. for $C_{15}H_8N_2O_2S_2$ (312.37): C, 57.68; H, 2.58; N, 8.97. Found: C, 57.4; H, 2.8; N, 8.7%. ^{1}H NMR (250.1 MHz, $CDCl_3$ solution): δ 3.95 (2 H, s, CH_2), 7.51 (1 H, dd, *J* 6.7 Hz and *J* 8.2 Hz, CH), 7.65-7.88 (3 H, m, 3 CH), 8.05 (1 H, d, *J* 6.8 Hz, CH), 8.24 (1 H, d, *J* 6.7 Hz, CH). ^{13}C NMR (62.5 MHz, $CDCl_3$ solution): 37.00 (CH_2), 125.41 (C), 126.19 (CH), 127.05 (C), 128.28 (CH), 129.63 (C), 130.17 and 131.25 (2 CH), 133.41 (C), 135.06 and 137.69 (2 CH), 155.91 (C), 164.75, 179.12, and 187.22 (2 C=O and C=S).

Electrode preparation

The PVC membrane preparation, involved the complete blending of the following compounds; 30 mg of powdered PVC, 63.5 mg of the NPOE plasticizer, 1.5 mg of the NaTPB additive and 5 mg of the ATTO ionophore in 5 mL of fresh THF. The resulting mixture was transferred into a glass dish (2 cm in diameter) and the solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3–5 mm i.d.) was dipped into the mixture, for about 10 s, so that a transparent membrane of about 0.3 mm thickness was formed. The tube was then removed from the mixture, kept at the room temperature for about 24 h, and then filled with an internal filling solution (1.0×10^{-3} mol L^{-1} of $SmCl_3$). Finally, the electrode was conditioned by soaking in a 1.0×10^{-2} mol L^{-1} $SmCl_3$ solution for 36 h.[36-46] A silver-silver chloride wire was used as the internal reference electrode.

The emf measurements

The equipments for the emf (electromotive force) measurements consisted of: *i*) Ag–AgCl | 3 mol L^{-1} KCl | internal solution, 1.0×10^{-3} mol L^{-1} $SmCl_3$ | PVC membrane | test solution | Hg–Hg_2Cl_2, KC1 (sat.), *ii*) a Corning ion analyzer with a 250 pH/mV meter and *iii*) a double-junction saturated calomel electrode (SCE, Philips) with the chamber filled with an ammonium nitrate solution. The activities were calculated according to the Debye–Huckel procedure.[47] The potential measurements were performed at 25.0 ^{0}C.

Results and Discussion

The ATTO-based electrode response to the Sm(III) ions

In preliminary investigations, ATTO was used as an ionophore in PVC membranes for a number of alkali, alkaline earth, transition and heavy metal ions, including sodium, potassium, magnesium, calcium, copper, nickel, cobalt, cadmium, lead, mercury, silver, lanthanum, cerium, ytterbium, gadolinium, terbium and samarium. The potential responses of the most sensitive ion-selective membrane electrodes, based on ATTO, are shown in Figure 2(a-b). Among the different tested cations, Sm^{3+} demonstrates the most sensitive response and seems to be suitably determined by the ATTO-PVC membrane. Therefore, this ionophore was selected as a suitable sensor material for Sm^{3+}-selective sensor.

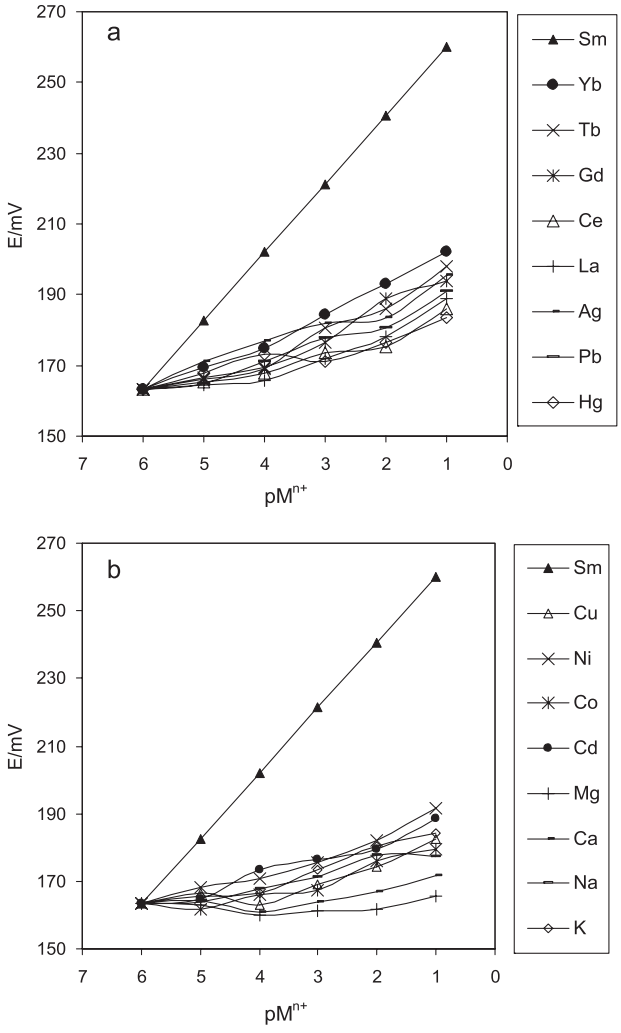

Figure 2. Potential responses of different ion-selective electrodes based on ATTO.

Membrane composition of the ATTO-based Sm(III) sensor

Some important features of PVC membranes, such as the properties of the plasticizer, the plasticizer/PVC ratio, the nature and amount of the ionophore and especially the nature and amount of the applied additives, are reported to significantly influence the sensitivity and selectivity of the ion-selective electrodes. The solvent mediator/PVC ratio in solvent polymeric membrane ion-selective electrodes is usually about 2, because polymeric films with such a plasticizer/PVC ratio will result in optimum physical properties and high mobilities of their constituents. In this study, the same plasticizer/PVC ratio (about 2) was found to be the most suitable, for the construction of the membrane sensors.[48-55] Thus, different compositions of ATTO-Sm(III)-selective membrane were optimized and the results are given in Table 1. Because the plasticizer nature affects the dielectric constant of the membrane phase, the mobility of the ionophore molecules

Table 1. Optimization of membrane ingredients

Electrode No.	Composition (wt.%), PVC 30%					Slope (mV *per* decade)	Conc. Range (mol L^{-1})
	ATTO	NaTPB	NPOE	DBP	BA		
1	3	0	67	0	0	9.8 ± 0.6	6.5×10^{-4}-5.0×10^{-1}
2	5	0	65	0	0	12.5 ± 0.3	2.3×10^{-4}-1.0×10^{-1}
3	5	1	62	0	0	16.4 ± 0.2	1.0×10^{-5}-1.0×10^{-1}
4	5	2	63	0	0	15.5 ± 0.3	1.0×10^{-5}-1.0×10^{-1}
5	5	1.5	63.5	0	0	19.3 ± 0.6	1.0×10^{-6}-1.0×10^{-1}
6	5	1.5	0	0	63.5	17.3 ± 0.4	1.0×10^{-6}-1.0×10^{-1}
7	5	1.5	0	63.5	0	16.7 ± 0.5	1.0×10^{-6}-1.0×10^{-1}

and the state of the ligand,[56] it was expected to play a key role in defining the selectivity, working concentration range and response time of the membrane electrode. From the three solvent mediators, it was found that NPOE with a dielectric constant of 23.9, is superior to the DBP and BA in the construction of the samarium membrane sensor. According to the reported data in Table 1, the membrane with a plasticizer/PVC ratio about 2.0 displayed the best performance. As it can be observed from the same table, the slope of the Sm(III) sensor is influenced by the amount of ATTO in the membrane composition (membrane Nos. 3, 4). Increasing ATTO up to 5% exhibited the best sensitivity (membrane No. 5).

The presence of lipophilic negatively charged additives in the PVC-base membrane sensors improves the potentiometric behavior of certain cation-selective sensors by reducing their ohmic resistance and improving the response behavior and selectivity, and in some cases, by catalyzing the exchange kinetics at the sample-membrane interface.[57-59] From Table 1, it is obvious that the presence of 1.5% sodium tetraphenyl borate, as a suitable lipophilic additive, considerably improves the samarium sensor sensitivity (No. 5 with a slope of 19.3 mV *per* decade). Clearly, in composition 5, the membrane incorporating 63.5% NPOE and 30% PVC, in the presence of 5% ATTO and 1.5% NaTPB, shows the optimium sensitivity, with a good Nernstian slope of 19.3 ± 0.6 mV *per* decade of Sm(III) concentrations (1.0×10^{-6} to 1.0×10^{-1} mol L^{-1}).

Calibration curve

The optimum equilibrium time for the membrane electrode, in the presence of 1.0×10^{-2} mol L^{-1} $SmCl_3$ was 12 h, after which it would generate stable potentials in contact with samarium solutions. The electrode had a linear response to the $SmCl_3$ ion activity in the range of 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} (Figure 3). The slope of the calibration graph was 19.3 ± 0.6 mV *per* decade. The detection limit, as determined from the intersection of

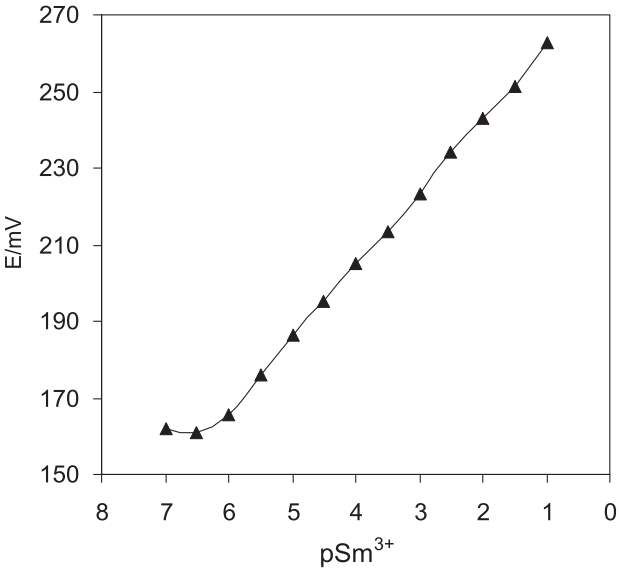

Figure 3. Calibration curve of samarium electrode based on ATTO.

the two extrapolated segments of the calibration graph, was $(5.5 \pm 0.3) \times 10^{-7}$ mol L^{-1}. The standard deviation of eight replicate measurements was ± 0.6 mV (RSD 3.1%). The recommended PVC-based membrane sensor could be used for at least ten weeks (using one hour per day and then, washed and dried). After this period the electrode slope reduced to some extent (from 19.3 to 17.5 mV *per* decade).

pH effect

In order to study the pH effect on the sensor performance, the potentials were determined in the pH range of 2.0-10.0 (concentrated NaOH or HCl was used for the pH adjustment) at two Sm^{3+} concentrations (1.0×10^{-3} and 1.0×10^{-2} mol L^{-1}). The corresponding results are depicted in Figure 4(a-b). Evidently, the potential remained constant from pH 3.5 to 7.5, beyond which some drifts in the potentials were observed. The observed drift at higher pH values could be attributed to the formation

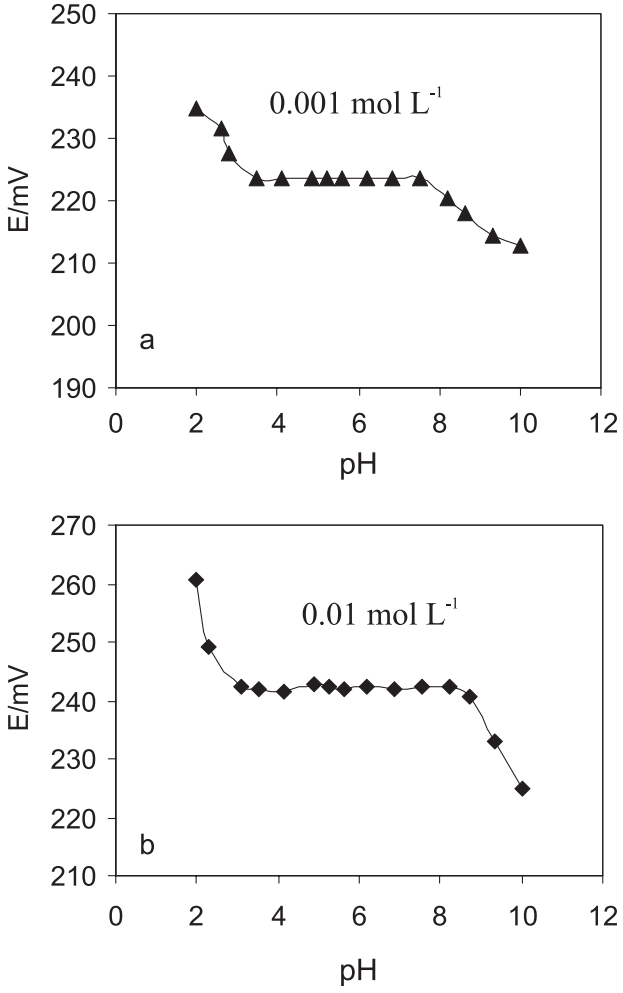

Figure 4. Effect of pH of the test solution (1.0×10^{-3} and 1.0×10^{-2} mol L^{-1} of Sm^{3+}) on the potential response of the Sm^{3+} ion-selective electrode.

of some Sm^{3+} hydroxyl complexes in the solution. At lower pH values, the potentials increased, indicating that the membrane sensor responded to protoned ions, as a result of some extent nitrogen atom protonation of the ionophore.

Dynamic response time and Sm(III) sensor life-time

The dynamic response time is an essential parameter for a sensor.[60] To evaluate this parameter, the average time required for the Sm(III) sensor to reach a ±1 mV potential of the final equilibrium value, after successive immersion into a series of Sm(III) ion solutions, each having a 10-fold concentration difference was measured. The potential *versus* time plot is shown in Figure 5. It is clear that over the entire concentration range the plasticized membrane electrode reaches its equilibrium responses in a short time (~10 s). Used for one hour every day (one hundred measurements), the membrane sensor lifetime is at least 10 weeks. After use during this period, the electrode was washed and kept dry.

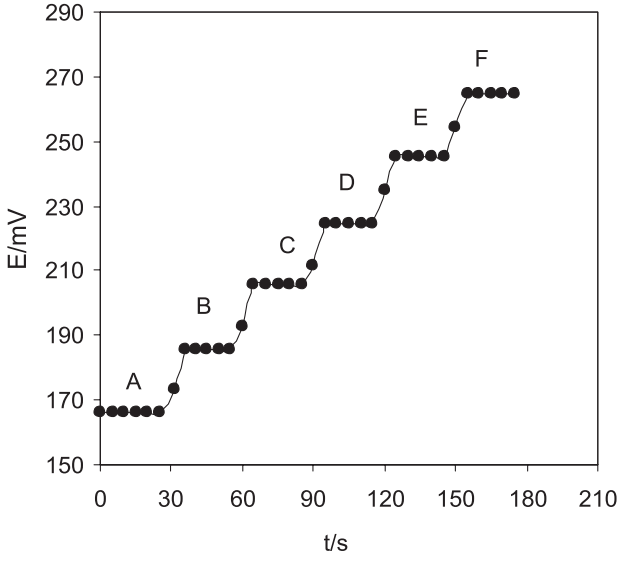

Figure 5. Dynamic response time of the samarium electrode for step changes in the concentration of Sm^{3+}: A) 1.0×10^{-6} mol L^{-1}, B) 1.0×10^{-5} mol L^{-1}, C) 1.0×10^{-4} mol L^{-1}, D) 1.0×10^{-3} mol L^{-1}, E) 1.0×10^{-2} mol L^{-1}, F) 1.0×10^{-1} mol L^{-1}.

During this period, the membrane sensor could be used without any measurable divergence in its potentials.

Sm(III) electrode selectivity

For the measurement of the selectivity coefficients, the matched potential method was used. According to the MPM,[61] a specified activity (concentration) of primary ions (A) is added to a reference solution and the potential is measured. In a separate experiment, interfering ions (B) are successively added to an identical reference solution, until the measured potential matches the one obtained before the primary ion addition. The MPM selectivity coefficient is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K^{MPM} = a_A/a_B$. The applied experimental conditions and the resulting values are listed in Table 2. For all tested ions, the selectivity coefficients are in the order of 5.5×10^{-3} or smaller, indicating they would not radically disturb

Table 2. Selectivity coefficients of various interfering ions (B)

Interfering ion	$K^{MPM}_{Sm^{3+},B}$	Interfering ion	$K^{MPM}_{Sm^{3+},B}$
Ce^{3+}	7.6×10^{-4}	K^{+}	9.5×10^{-4}
Tb^{3+}	3.5×10^{-3}	Ag^{+}	1.5×10^{-3}
La^{3+}	8.8×10^{-4}	Hg^{2+}	8.5×10^{-4}
Yb^{3+}	5.5×10^{-3}	Pb^{2+}	1.0×10^{-3}
Gd^{3+}	5.0×10^{-3}	Cd^{2+}	1.0×10^{-3}
Mg^{2+}	1.0×10^{-4}	Cu^{2+}	7.7×10^{-4}
Ca^{2+}	3.2×10^{-4}	Co^{2+}	8.0×10^{-4}
Na^{+}	9.1×10^{-4}	Ni^{2+}	1.0×10^{-3}
Fe^{3+}	1.0×10^{-3}	Al^{3+}	3.0×10^{-3}

Table 3. Comparison of selectivity coefficients, detection limit, response time and linearity range of proposed Sm(III) sensor and the previously reported Sm(III) ion-selective electrodes

	Reference 15	Reference 16	Reference 17	Reference 19	This work
Linearity rang / (mol L^{-1})	1.0×10^{-5}-1.0×10^{-1}	1.0×10^{-6}-1.0×10^{-1}	1.0×10^{-5}-1.0×10^{-1}	1.0×10^{-5}-1.0×10^{-1}	1.0×10^{-6}-1.0×10^{-1}
Detection limit / (mol L^{-1})	8.0×10^{-6}	6.0×10^{-7}	3.1×10^{-6}	1.0×10^{-5}	5.5×10^{-7}
Response time / (s)	20	<10	~10	~10	~10
Selectivity coefficients	MPM	MPM	MPM	FIM	MPM
Na^{+}	-3.50	-3.12	-2.20	-0.20	-3.04
K^{+}	-3.39	-3.07	-2.25	__	-3.02
Mg^{2+}	-2.72	-2.60	-1.57	__	-4.00
Ca^{2+}	-2.92	-2.70	-2.28	-0.30	-3.50
Ni^{2+}	-2.38	-2.68	-1.20	__	-3.00
Cu^{2+}	-2.51	-2.82	-1.32	__	-3.11
Co^{2+}	-2.28	-3.07	-1.08	__	-3.10
Cd^{2+}	-2.72	__	-1.04	__	-3.00
Pb^{2+}	-1.04	-2.04	-1.35	__	-3.00
Hg^{2+}	__	-2.66	-2.06	__	-3.07
Ag^{+}	-2.41	-2.04	-1.10	__	-2.82
La^{3+}	-1.27	-2.40	-1.85	-0.40	-3.05
Yb^{3+}	__	__	__	-0.40	-2.26
Gd^{3+}	-1.06	-2.40	-1.10	__	-2.30
Tb^{3+}	__	__	__	-0.40	-2.45
Ce^{3+}	-1.09	-2.10	-1.85	-0.51	-3.12

Table 4. Determination of the concentration of Sm(III) in tap water and river water samples by use of the proposed electrode

Sample	Added / (mg mL^{-1})	Found[a] / (mg mL^{-1})	Recovery / (%)
River water[b]	0.1	0.11 ± 0.02	110
	0.3	0.32 ± 0.05	106.6
	0.5	0.54 ± 0.07	108
Tap water[b]	0.1	0.11 ± 0.01	110
	0.3	0.31 ± 0.04	103.3
	0.5	0.52 ± 0.03	104

[a] Results are based on three measurements; [b] The permitted level of the samarium in the water is 0.12 mg mL^{-1}.

Table 5. Recovery of Sm(III) ions from binary mixtures

Sm(III) / (ppm)	Added cation / (ppm)	Recovery / (%)
10	La^{3+} (100)	100.4[a] ± 0.3
10	Ce^{3+} (100)	98.4 ± 0.5
10	Tb^{3+} (100)	102.3 ± 0.6
10	Yb^{3+} (100)	98.8 ± 0.4
10	Gd^{3+} (100)	99.9 ± 0.5
10	Ag^{+} (100)	103.2 ± 0.4
10	Pb^{2+} (100)	101.7 ± 0.7
10	Cd^{2+} (100)	101.6 ± 0.3
10	Co^{2+} (100)	99.6 ± 0.6
10	Ni^{2+} (100)	100.5 ± 0.5
10	Cu^{2+} (100)	100.1 ± 0.3
10	Zn^{2+} (100)	102.2 ± 0.2
10	Mg^{2+} (100)	101.8 ± 0.3
10	Ca^{2+} (100)	98.8 ± 0.5
10	K^{+} (100)	102.1 ± 0.7
10	Na^{+} (100)	100.4 ± 0.5

[a] Results are based on three measurements.

the function of the developed Sm(III) membrane sensor. Therefore, the electrode can be used for the detection of Sm(III) ion in the presence of certain interfering ions.

The characteristics of the samarium membrane sensor were compared with those of the best samarium electrodes reported in the literature[21-23,25] (Table 3). It can be concluded that this sensor, in terms of selectivity, detection limit, response time and dynamic concentration range, is superior to all formerly reported samarium sensors.

Analytical application

Using the proposed electrode as an indicator, the titration of 25 mL of 10^{-4} mol L^{-1} Sm(III) ions against 10^{-2} mol L^{-1} EDTA was performed. The resulting titration curve is depicted in Figure 6, where it can be seen that the sensor can monitor the amount of samarium ions well.

This electrode was also successfully applied to the direct samarium detection in tap water; river water and binary mixture samples. The resulting data are summarized in Table 4 and 5, respectively. It was found that the accuracy of samarium detection in different solution samples is almost quantitative.

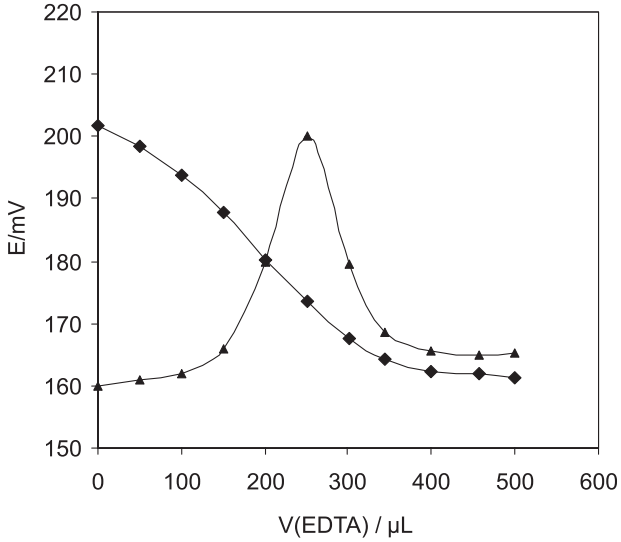

Figure 6. Potential titration curves of 25.0 mL 1.0×10^{-4} mol L^{-1} Sm(III) solution with 1.0×10^{-2} mol L^{-1} of EDTA and its first order derivative.

The electrode was also applied to the determination of Sm(III) in a permanent magnet material $SmCo_5$. To do this first, 0.1 g of this compound was completely dissolved in 5.0 mL of a 0.1 mol L^{-1} sulfuric acid. The pH of the resulting solution was then adjusted to 4.5 with 5.0 mL of 0.1 mol L^{-1} sodium acetate–acetic acid buffer solution and diluted to the mark with distilled water in a 100 mL calibrated volumetric flask. Finally, the samarium(III) content of solution was determined by the proposed sensor, using the calibration method. The results obtained from four replicate measurements (33.8 ± 0.8%), were found to be in satisfactory agreement with the certified value of 33%.

Conclusions

This study reveals that a potentiometric PVC-constructed membrane sensor, which is based on the ATTO functions, consists of an excellent Sm^{3+} selective sensor. The proposed samarium sensor in the terms of selectivity coefficients and detection limit is superior to all previously reported samarium sensors. The selectivity coefficients of the sensor for the common alkaline metal, transition and lanthanide ions (except Gd^{3+}) are very low and makes it as suitable device for the fast determination of this ion in the presence of considerable concentrations of common interfering ions in the real samples such as river and tap waters and samarium alloy.

References

1. Parker, S. P.; *Concise Encyclopedia of Science and Technology*, **1984**, McGraw-Hill, New York, p. 390.
2. Kirk, O. R.; Othmer, F. D.; *Encyclopedia of Chemical Technology*, **1982**, Vol. 19, Wiley, p. 851.
3. Haiduc, I.; Silvestru, C. *Coord. Chem. Rev.* **1990**, 99, 253.
4. Yongxing, W.; Xiaorong, W.; Zichum, H. *Bull. Environ. Contamin. Toxicol.* **2000**, 64, 611.
5. Zheng, H. L.; Zhao, Z. Q.; Zhang, C. C.; Feang G. Z.; Ke, Z. L.; Su, M. G. *BioMtetals* **2000**, 13, 157.
6. Hampel, C. A.; Book, R. The encyclopedia of the chemical elements, Corporation, **1968,** New York.
7. Biju, V.M.; Rao, T.P.; *Anal. Sci.* **2001,**17, 1343.
8. Hrdlicka, A.; Havel, J.; Moreno, C.; Valiente, M. *Anal. Sci.* **1991**, 7, 925.
9. Houk, R. S.; Fassel, V.A.; Reach, G.D.; Svec, H.J. *Anal. Chem.* **1980**, 52, 2283.
10. Mazzucotelli, A.; DePaz, F.; Magi, E.; B. Frache, *Anal. Sci.* **1992**, 8, 189.
11. Masuda, A.; Nomura, N.; Tanaka, T.; *Geockim. Cosmochim. Arla* **1973**, 37, 239.
12. Marsh, S. F. *Anal. Chem.* **1967**, 39, 641.
13. Cornell, D. H. *Pure Appl Chem.* **1993**, 65, 2453.
14. http://www.lenntech.com/Periodic-chart-elements/Sm-en.htm, Permanent, Last update: Copyright © 1998-2006
15. http://en.wikipedia.org/wiki/Samarium, Permanent, Last update: This page was last modified 10:20, 20 January 2007.
16. Song, K.; S.; Cha, H.; K.; Lee, J.; *J. Anal. At. Spectrom.* **1998**, *13*, 1207.
17. Huang, H.; G.; Gao, X.; X.; Hu, Y.; *Bunseki Kagaku* **1990**, 39, 233.
18. Rusakova, N.; V.; Meshkova, S.; B.; Poluektov, N.; S.; *Industrial Laboratory* **1989**, *55*, 664.
19. Hidaka H.; Ebihara M.; Shima M.; *Anal. Chem.* **1995**, *67*, 1437.
20. Ganjali, M. R.; Rezapour, M.; Pourjavid, M.; R.; Haghgoo, S.; *Anal. Sci.* **2004**, *20*, 1007.
21. Shamsipur, M.; Hosseini, M.; Alizadeh, K.; Talebpour, Z.; Mousavi, M.; F.; Ganjali, M.; R.; Arca, M.; Lippolis, V.; *Anal. Chem.* **2003**, *75*, 5680.
22. Ganjali, M.; R.; Pourjavid, M.; R.; Rezapour, M.; Haghgoo, S.; *Sens. Actuators B* **2003**, *89*, 21.
23. Shamsipur, M.; Hosseini, M.; Alizadeh, K.; Eskandari, M.; M.; Sharghi, H.; Mousavi, M. F.; Ganjali, M.; R.; *Anal. Chim. Acta.* **2003**, *486*, 93.
24. Chowdhury, D.; A.; Ogata, T.; Kamata, S.; *Anal. Chem.* **1996**, *68*, 366.
25. Mittal, S.; K.; Sharma, H.; K.; Kumar, A.; S.; K.; *Sensors* **2004**, *4*, 125.
26. Zamani, H.; A.; Rajabzadeh, G.; Firouz, A.; Ariaii-Rad, A.; A.; *J. Braz. Chem. Soc.* **2005**, *16*, 1061.
27. Ganjali, M.; R.; Zamani, H.; A.; Norouzi, P.; Adib, M.; Rezapour, M.; Aceedy, M.; *Bull. Korean. Chem. Soc.* **2005**, *26*, 579.
28. Ganjali, M.; R.; Zamani, H.; A.; Norouzi, P.; Adib, M.; Accedy, M.; *Acta Chim. Slov.* **2005**, *52*, 309.

29. Zamani, H.; A.; Rajabzadeh, G.; Ganjali, M.; R.; Khatami, S.; M.; *Electroanalysis* **2005**, *17*, 2260.
30. Zamani, H.; A.; Ganjali, M.; R.; Pooyamanesh, M.; J.; *J. Braz. Chem. Soc.* **2006**, *17*, 149.
31. Zamani, H.; A.; Rajabzadeh, G.; Ganjali, M.; R.; *Sens. Actuators B* **2006**, *119*, 41.
32. Zamani, H.; A.; Malekzadegan, F.; Ganjali, M.; R.; *Anal. Chim. Acta.* **2006**, *555*, 336.
33. Zamani, H.; A.; Ganjali, M.; R.; Adib, M.; *Sens. Actuators B* **2007**, *120*, 545.
34. Zamani, H.; A.; Rajabzadeh, G.; Ganjali, M.; R.; *J. Braz. Chem. Soc.* **2006**, *17*, 1297.
35. Zamani, H.; A.; Abedini-Torghabeh, J.; Ganjali, M.; R.; *Electroanalysis*, **2006**, *18*, 888.
36. Zamani, H. A.; Abedini-Torghabeh, J.; Ganjali, M. R.; *Bull. Korean Chem. Soc.* **2006**, *27*, 835.
37. Zamani, H. A.; Ganjali, M. R.; Norouzi, P.; Adib, M.; Aceedy, M.; *Anal. Sci.* **2006**, *22*, 943.
38. Ganjali, M.; R.; Kiani-Anbouhi, R.; Shamsipur, M.; Poursaberi, T.; Salavati-Niasari, M.; Talebpour, Z.; Emami, M. *Electroanalysis* **2004**, *12*, 1002.
39. Ganjali, M.; R.; Rezapour, M.; Norouzi, P.; Salavati-Niasari, M.; *Electroanalysis* **2005**, *22*, 2032.
40. Ganjali, M.; R.; Rasoolipour, S.; Rezapour, M.; Norouzi, P.; Tajarodi, A.; Hanifehpour, Y.; *Electroanalysis* **2005**, *17*, 1534.
41. Ganjali, M.; R.; Ravanshad, J.; Hosseini, M.; Salavati-Niasari, M.; Pourjavid, M.; R.; Baezzate, M.; R.; *Electroanalysis* **2004**, *16*, 1771.
42. Ganjali, M.; R.; Shirvani-Arani, S.; Nourozi, P.; Salimzadeh, D.; Faal-Rastegar, M.; Moghimi, A.; *Electroanalysis* **2004**, *12*, 1009.
43. Ganjali, M.; R.; Pourjavid, M.; R.; Rezapour, M.; Poursaberi, T.; Daftari, A.; Salavati-Niasari, M.; *Electroanalysis* **2004**, *11*, 922.
44. Ganjali, M.; R.; Norouzi, P.; Golmohammadi, M.; Rezapour, M.; Salavati-Niasari, M.; *Electroanalysis* **2004**, *11*, 910.
45. Ganjali, M. R.; Akbar, V.; Norouzi, P.; Moghimi, A.; Sepehrifard, A.; *Electroanalysis* **2005**, *10*, 895.
46. Ganjali, M.; R.; Fathi, M.; R.; Rahmani, H.; Pirelahi, H.; *Electroanalysis* **2000**, *14*, 1138.
47. Kamata, S.; Bhale, A.; Fukunaga, Y.; Murata, A.; *Anal. Chem.* **1988**, *60*, 2464.
48. Rostazin, T.; Bakker, E.; Suzuki, K.; Simon, W.; *Anal. Chim. Acta* **1993**, *280*, 197.
49. Teixeria, M. F. S.; Pinto, A. Z.; Fatibello-Filho, O.; *Talanta* **1997**, *45*, 249.
50. Teixeria, M. F. S.; Fatibello-Filho, O.; Ramos, L. A.; *Quim. Nova* **2005**, *28*, 817.
51. Teixeria, M. F. S.; Fatibello-Filho, O.; *J. Braz. Chem. Soc.* **1996**, *7*, 233.
52. Ammann, E.; Pretsch, E.; Simon, W.; Lindner, E.; Bezegh, A.; Pungor, E.; *Anal. Chim. Acta* **1985**, *171*, 119.
53. Ganjali, M.; R.; Daftari, A.; Norouzi, P.; Salavati-Niasari, M.; *Anal. Lett.* **2003**, *36*, 1511.
54. Ganjali, M.; R.; Qomi, M.; Daftari, A.; Norouzi, P.; Salavati-Niasari, M.; Rabbani, M.; *Sens. Actuators B* **2004**, *98*, 92.
55. Ganjali, M.; R.; Mizani, F.; Emami, M.; Darjezini, M.; Darvich, M.; R.; Yousefi, M.; *Anal. Sci.* **2004**, *20*, 531.
56. Bakker, E.; Buhlmann, P.; Pretsch, E.; *Electroanalysis* **1999**, *11*, 915.
57. Bakker, E.; Bühlmann, P.; Pretsch, E.; *Chem. Rev.* **1997**, *97*, 3083.
58. Malinowska, E.; *Analyst* **1990**, *115*, 1085.
59. Koryta, J.; *Anal. Chim. Acta* **1990**, *233*, 1.
60. Matysik, S.; Matysik, F.; M.; Mattusch, J.; Einicke, W.; D.; *Electroanalysis* **1998**, *10*, 98.
61. Umezawa, Y.; Umezawa, K.; Sato, H.; *Pure Appl. Chem.* **1995**, *67*, 507.

Received: May 31, 2006
Web Release Date: January 26, 2007