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## **Investigation of interfering ions effect on a gadolinium(III) PVC membrane sensor**

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### **ABSTRACT**

*A PVC-membrane ion-selective electrode was constructed for quantitative monitoring of gadolinium(III) ion based on 3-methyl-1H-1,2,4-triazole-5-ylhydrosulfide (MTY) as an ion carrier. The electrode performance includes a Nernstian slope of  $19.8 \pm 0.4$  mV per decade across a wide concentration range between  $1.0 \times 10^{-7}$  and  $1.0 \times 10^{-2}$  M and a detection limit of  $7.3 \times 10^{-8}$  M. The best performance was obtained with a membrane composition of 30% poly(vinyl chloride), 66% nitrobenzene (NB), 2% sodium tetraphenyl borate (NaTPB) and 2% MTY. This sensor shows very good selectivity and sensitivity towards gadolinium ion over a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. The sensor revealed a great enhancement in selectivity coefficients for gadolinium ions, in comparison to the previously reported gadolinium sensors. For testing applicability of the sensor in real sample analysis, it was successfully applied to the  $F^-$  ions determination in some mouth washing solutions.*

**Keywords:** Potentiometry, Sensor, Ion selective electrode, PVC membrane.

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### **INTRODUCTION**

Construction and application of ion selective electrode as a potentiometric sensor offers interesting advantages such as simplicity, speed, relatively fast response, low cost, wide linear dynamic range and ease of preparation and procedures. These characteristics have inevitably led to the preparation of numerous sensors for several ionic species, and the list of available electrodes has grown substantially over the past years [1]. Thus, they have been widely applied as ionophores for construction membrane sensor for metal ions. Due to their ease of preparation,

simple operation, fast response time, reasonable selectivity and wide linear working range, the solvent polymeric membrane ion-selective electrodes incorporating suitable ion-carriers have been shown to be very useful tools for these purposes. Gadolinium is one of the more abundant rare-earth elements. It is never found as free element in nature, but it is contained in many rare minerals. Gadolinium and other lanthanide oxides are widely used in the preparation of optical glasses, glass fibers for optical purposes, gasoline-cracking catalysts, polishing compounds and carbon arcs, and in the iron and steel industries to remove sulfur, carbon, and other electronegative elements from iron and steel [2]. There are some reports on ion selective electrode for gadolinium ion [3-8]. Recently, several electrodes have been reported for anions and metal ions [9-25].

## EXPERIMENTAL SECTION

### Reagents

Three companies provided the necessary chemicals (of analytical reagent grade) for the experimental part of the study: a) the Merck Co., supplying the dibutylphthalate (DBP), nitrobenzene (NB), the chloride and nitrate salts of the used cations and acetophenon (AP), b) the Aldrich Co., which supplied the chloride and nitrate salts of the used cations, c) the Fluka Co., providing the high-molecular weight polyvinylchloride and tetrahydrofuran (THF). The chloride and nitrate salts of the used cations were also purchased from Merck and Aldrich at the highest available purity and were submitted to no further modification. The ionophore MTY was synthesized as described elsewhere [26-29]. All solutions were prepared using doubly distilled deionized water.

### Electrode preparation

The general procedure to prepare the PVC membrane was to mix thoroughly, 30 mg of PVC, 2 mg of MTY, 2 mg of NaTPB and 66 mg of NB. Then the mixture was dissolved in 3 mL of dry freshly distilled THF. The resulting clear mixture was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (5 mm i.d.) was dipped into the mixture for about 5 s, so that a transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 12 h [30-32]. The tube was then filled with internal solution ( $1.0 \times 10^{-3}$  M  $\text{GdCl}_3$ ). The electrode was finally conditioned for 24 h by soaking in a solution containing  $1.0 \times 10^{-3}$  M  $\text{GdCl}_3$  solution. A silver/silver chloride coated wire was used as an internal reference electrode.

### The emf measurements

All emf measurements were carried out with the following assembly:

$\text{Ag}-\text{AgCl} | 1.0 \times 10^{-3}$  M  $\text{GdCl}_3$  | PVC membrane: test solution |  $\text{Hg}-\text{Hg}_2\text{Cl}_2$ , KCl (satd).

A Corning ion analyser 250 pH/mV meter was used for the potential measurements at 25.0 °C. The activities were calculated according to the Debye–Huckel procedure.

## RESULTS AND DISCUSSION

In order to check the MTY suitability as an ion carrier for different metal ions, it was used to prepare PVC membrane ion-selective electrodes in preliminary experiments for a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. Among different metal

ions tested,  $\text{Gd}^{3+}$  ion displays a strong response (with a slope of  $19.8 \pm 0.4$  mV per decade) to the MTY-based membrane sensors in comparison with the other tested cations. In the next step, membrane ingredients effect (the nature and the amount of the ionophore, the nature and the amount of the used additive and the kind of plasticizer) were investigated on the potential response of the  $\text{Gd}^{3+}$  electrode. The membrane sensor with composition of 30% PVC; 66% NB; 2% NaTPB, and 2% MTY exhibits the best performance.

The measuring range of an ion-selective electrode includes the linear part of the calibration graph (emf vs.  $\text{pGd}^{3+}$ ). The slope and the linear range of the resulting calibration graph were  $19.8 \pm 0.4$  mV per decade and  $1.0 \times 10^{-7}$ - $1.0 \times 10^{-2}$  M, respectively. The limit of detection, defined as the  $\text{Gd}^{3+}$  ion concentration obtained when the linear region of the calibration graph was extrapolated to the base line potential, was  $7.3 \times 10^{-8}$  M.

The selectivity behavior is obviously one of the most important characteristics of an ion-selective electrode, determining the feasibility of a reliable measurement in the target sample. To investigate the membrane electrode selectivity, its potential response was monitored in the presence of various interfering foreign cations using the matched potential method (MPM) [36-38]. According to the MPM, the selectivity coefficient is defined as the activity (concentration) ratio of the primary ion and the interfering ion, which gives the same potential change in a reference solution. Thus, the potential change should be measured upon changing the primary ion activity. Then, the interfering ion would be added to an identical reference solution until the same potential change would be obtained. The matched potential method selectivity coefficient,  $K^{\text{MPM}}$ , is then given by the resulting primary ion to the interfering ion activity (concentration) ratio,  $K^{\text{MPM}} = a_A/a_B$ . The resulting potentiometric selectivity coefficients values are summarized in Table 1. The data given in Table 1, revealed the selectivity coefficients of the electrode for all the diverse ions are in the order of  $5.5 \times 10^{-3}$  or smaller, indicating they would not significantly disturb the function of the Gd(III) selective membrane sensor. The surprisingly high selectivity of the membrane electrode for Gd(III) ions over other cations used, most probably arises from the strong tendency of the carrier molecules for Gd(III) ions. Table 2 compares the linearity range, detection limit and selectivity coefficients of the suggested sensor with the best previously reported Gd(III) sensors [3-8]. It is evident that the newly developed sensor is superior to the formerly reported Gd(III) sensors in terms of selectivity, detection limit and dynamic concentration range.

The electrode was used in the potentiometric determination of fluoride ions in two mouth wash samples. The results were derived from triplicate measurements and are listed in Table 3. From Table 3, there is a satisfactory agreement between the declared fluoride content and the determined values.

Table 1: Selectivity coefficients of various interfering ions

Interfering ions	$K_{Gd^{3+},B}^{MPM}$	Interfering ions	$K_{Gd^{3+},B}^{MPM}$
Yd <sup>3+</sup>	$4.3 \times 10^{-3}$	Fe <sup>3+</sup>	$3.9 \times 10^{-3}$
Tb <sup>3+</sup>	$5.5 \times 10^{-3}$	Cr <sup>3+</sup>	$4.6 \times 10^{-3}$
Ho <sup>3+</sup>	$8.7 \times 10^{-4}$	K <sup>+</sup>	$8.3 \times 10^{-4}$
La <sup>3+</sup>	$7.2 \times 10^{-4}$	Na <sup>+</sup>	$7.8 \times 10^{-4}$
Dy <sup>3+</sup>	$2.6 \times 10^{-3}$	Ca <sup>2+</sup>	$1.0 \times 10^{-3}$
Lu <sup>3+</sup>	$3.1 \times 10^{-3}$	Co <sup>2+</sup>	$3.5 \times 10^{-3}$
Pr <sup>3+</sup>	$8.5 \times 10^{-4}$	Ni <sup>2+</sup>	$3.3 \times 10^{-3}$
Tm <sup>3+</sup>	$4.2 \times 10^{-3}$	Cd <sup>2+</sup>	$4.7 \times 10^{-3}$
Nd <sup>3+</sup>	$2.4 \times 10^{-3}$	Pb <sup>2+</sup>	$2.8 \times 10^{-3}$

Table 2: Comparison table of the characterization of reported Gd(III) potentiometric electrodes

Character / reference	Ref. 3	Ref. 4	Ref. 5	Ref. 6	Ref. 7	Ref. 8	This work
LR (mol L <sup>-1</sup> )	$1.0 \times 10^{-5}$ - $1.0 \times 10^{-1}$	$3.0 \times 10^{-7}$ - $1.0 \times 10^{-1}$	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$	$1.0 \times 10^{-5}$ - $1.0 \times 10^{-1}$	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$	$2.0 \times 10^{-5}$ - $1.0 \times 10^{-1}$	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-2}$
DL (mol L <sup>-1</sup> )	$5.0 \times 10^{-6}$	$3.0 \times 10^{-7}$	$5.8 \times 10^{-7}$	$3.0 \times 10^{-6}$	$7.0 \times 10^{-7}$	$5.0 \times 10^{-6}$	$7.3 \times 10^{-8}$
Slope (mV/decade)	19.3±0.3	19.9±0.3	19.8±0.2	19.8±0.3	19.4±0.4	30.0	19.8 ±0.4
Log K <sub>sel</sub> >-3	La <sup>3+</sup> , Sm <sup>3+</sup> , Ce <sup>3+</sup> , Co <sup>2+</sup> , Cd <sup>2+</sup> , Pb <sup>2+</sup> , Cu <sup>2+</sup> , Ag <sup>+</sup>	Sm <sup>3+</sup> , Eu <sup>3+</sup>	Hg <sup>2+</sup> , Cd <sup>2+</sup> , Pb <sup>2+</sup> , Yb <sup>2+</sup>	La <sup>3+</sup> , Sm <sup>3+</sup> , Eu <sup>3+</sup> , Yb <sup>3+</sup> , Dy <sup>3+</sup> , Cu <sup>2+</sup>	Cu <sup>2+</sup> , Li <sup>+</sup>	Not available	-

Table 3: Fluoride ions determination in mouth wash solutions

Sample	Labeled (ppm)	Found ISE <sup>a</sup> (ppm)
Sodium fluoride mouth wash solution (Aquafresh, Brentford, U.K.)	1350	(1378 ± 21)
Sodium fluoride mouth wash solution (Eurodont, DuroDont GmbH)	1450	(1488 ± 18)

a. Suggested Gd<sup>3+</sup> sensor

b. Results are based on three measurements

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### REFERENCES

- [1] P Bühlmann; E Pretsch; E Backer. *Chem. Rev.* **1998**, 98, 1593.
- [2] OR Kirk; FD Othmer. *Encyclopedia of Chemical Technology.* **1982**, Vol. 19, Wiley, p. 851
- [3] MR Ganjali; M Tahami; M Shamsipur; T Poursaberi; S Haghgoo; M Hosseini. *Electroanalysis* **2003**, 12, 1038.
- [4] MR Ganjali; P Norouzi; T Alizadeh; A Tajarodi; Y Hanifehpour. *Sens. Actuators B* **2007**, 120, 487.
- [5] HA Zamani; G Rajabzadeh; MR Ganjali; P Norouzi. *Anal. Chim. Acta* **2007**, 598, 51.

- [6] MR Ganjali; M Emami; M Rezapour; M Shamsipur; B Maddah; M Salavati-Niasari; M Hosseini; Z Talebpoui. *Anal. Chim. Acta* **2003**, 495, 51.
- [7] MR Ganjali; M Rezapour; P Norouzi; M Salavati-Niasari. *Electroanalysis* **2005**, 17, 2032.
- [8] HK Sharma; N Sharma. *E-J. Chem.* **2009**, 6, 1139.
- [9] HA Zamani; MT Hamed-Mosavian; E Aminzadeh; MR Ganjali; M Ghaemy; H Behmadi; F Faridbod. *Desalination* **2010**, 250, 56.
- [10] HA Zamani; G Rajabzadeh; MR Ganjali; *Sensor Lett.*, **2009**, 7, 114.
- [11] HA Zamani; MS Zabihi; M Rohani; A Zangeneh-Asadabadi; MR Ganjali; F Faridbod; S Meghdadi. *Mater. Sci. Eng. C* **2011**, 31, 409.
- [12] HA Zamani; A Arvinfar; F Rahimi; A Imani; MR Ganjali; S Meghdadi. *Mater. Sci. Eng. C* **2011**, 31, 307.
- [13] H Behmadi; HA Zamani; MR Ganjali; P Norouzi. *Electrochim. Acta* **2007**, 53, 1870.
- [14] HA Zamani; M Nekoei; M Mohammadhosseini; MR Ganjali. *Mater. Sci. Eng. C* **2010**, 30, 480.
- [15] HA Zamani; MR Ganjali; P Norouzi; M Adib; M Aceedy. *Anal. Sci.*, **2006**, 22, 943.
- [16] MR Abedi; HA Zamani; MR Ganjali; P Norouzi. *Sensor Lett.*, **2007**, 5, 516.
- [17] HA Zamani. *Anal. Lett.*, **2009**, 42, 615.
- [18] MR Abedi; HA Zamani. *Anal. Lett.*, **2008**, 41, 2251.
- [19] HA Zamani; MR Ganjali; P Norouzi; M Adib. *Sensor Lett.*, **2007**, 5, 522.
- [20] HA Zamani; MR Ganjali; P Norouzi; A Tadjarodi; E Shahsavani. *Mater. Sci. Eng. C* **2008**, 28, 1489.
- [21] HA Zamani; G Rajabzadeh; MR Ganjali. *Talanta* **2007**, 72, 1093.
- [22] HA Zamani; MR Ganjali; M Salavati-Niasari. *Transition. Met. Chem.*, **2008**, 33, 995.
- [23] HA Zamani; M Mohammadhosseini; M Nekoei; MR Ganjali. *Sensor Lett.*, **2010**, 8, 303.
- [24] M Masrournia; HA Zamani; HA Mirrashid; MR Ganjali; F Faridbod. *Mater. Sci. Eng. C* **2011**, 31, 574.
- [25] HA Zamani; A Imani; A Arvinfar; F Rahimi; MR Ganjali; F Faridbod; S Meghdadi. *Mater. Sci. Eng. C* **2011**, 31, 588.
- [26] RG Jones; C Ainsworth. *JACS* **1955**, 77, 1538.
- [27] CK Patel; CS Rami; B Panigrahi; CN Patel. *J. Chem. Pharm. Res.* **2010**, 2, 73.
- [28] S Chandra; BN Ghogare; LK Gupta; CP Shinde. *J. Chem. Pharm. Res.* **2010**, 2, 240.
- [29] SK Srivastava; S Verma; SD Srivastava. *J. Chem. Pharm. Res.* **2010**, 2, 270.
- [30] HA Zamani; M Rohani; A Zangeneh-Asadabadi; MS Zabihi; MR Ganjali; M Salavati-Niasari. *Mater. Sci. Eng. C* **2010**, 30, 917.
- [31] HA Zamani; G Rajabzadeh; M Masrornia; A Dejbord; MR Ganjali; N Seifi. *Desalination* **2009**, 249, 560.
- [32] HA Zamani; H Ghahremani; H Behmadi. *J. Chem. Pharm. Res.* **2010**, 2, 328.
- [33] MR Ganjali; F Faridbod; P Norouzi; M Adib. *Sens. Actuators B* **2006**, 120, 119.
- [34] MR Ganjali; P Norouzi; A Atrian; F Faridbod; S Meghdadi; M. Giahi. *Mater. Sci. Eng. C* **2009**, 29, 205.
- [35] VK Gupta, RN Goyal; RA Sharma. *Anal. Chim. Acta* **2009**, 647, 66.
- [36] Y Umezawa; K Umezawa; H Sato. *Pure Appl. Chem.*, **1995**, 67, 507.
- [37] HA Zamani; MT Hamed-Mosavian; E Hamidfar; MR Ganjali; P Norouzi. *Mater. Sci. Eng. C* **2008**, 28, 1551.
- [38] HA Zamani; MR Ganjali; P Norouzi; M Adib. *Mater. Sci. Eng. C* **2008**, 28, 157.