

A New Potentiometric Sensor for Determination of Cesium ion in Environmental samples

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Received 4 April 2010;

Revised 13 July 2010;

Accepted 25 July 2010

ABSTRACT: A new cesium ion selective PVC membrane based on parent calix [4] arene was developed for potentiometric determination of cesium in environmental samples. The electrode based on p-5,11,17,23tetra(tert-butyl)25,26,27,28-tetrahydroxy calix[4]arene(THC) as ionophor ,dibutyl phthalate (DBP)as plasticizer ,sodium tetra phenyl borate(NaTPB)and oleic acid as lipophilic salt and additive showed the best performance. The electrode exhibits a good Nernstian response in a concentration range of 1×10^{-1} - 3.16×10^{-5} M of cesium, with a slope of 58.5 ± 0.6 mv per decade and a detection limit of 1.58×10^{-5} M.It exhibits a good selectivity for cesium in comparison with alkali, alkaline earth, and some transition metal ions. The electrode response and selectivity remained almost unchanged for more than a month. The effect of membrane composition, pH and concentration of internal solution on the potential response of the electrode were also studied. The applicability of the electrode to real samples was also assessed.

Key words: Potentiometric determination, Cesium ion-selective electrode, Environmental samples

INTRODUCTION

Lots of studies have discussed different aspects of water bodies pollution with different kinds of metals (Abdullahi *et al.*, 2009, Ahmad *et al.*, 2010, Nasrabadi *et al.*, 2010, Taghinia *et al.*, 2010, Nasrabadi *et al.*, 2009, Chibunda *et al.*, 2010, Dhir and Kumar, 2010, Baghvand *et al.*, 2010). Cesium, being one of the heavy alkali metals, is also one of the most reactive and is highly explosive when it comes in contact with water and hydrogen released, causing ignition, and violent explosion. Cesium hydroxide is extremely strong base and can etch glass.

Cesium compounds are rarely encountered by most persons. All Cesium compounds should be regarded as mildly toxic because of its chemical similarity to Potassium. Large amounts cause hyperirritability and spasms, but such amounts would not ordinarily encountered in natural sources. Humans may be exposed to Cesium by breathing, drinking or eating. In air the levels of Cesium are generally low, but radioactive Cesium has been detected at some level in surface water and in many types of foods (Lee and Mohamed, 2009, Ahmad *et al.*, 2010, Karbassi *et al.*, 2007). The amount of

Cesium in foods and drinks depends upon the emission of radioactive Cesium through nuclear power plants, mainly through accidents. These accidents have not occurred since the Chernobyl disaster in 1986. People that work in the nuclear power industry may be exposed to higher levels of Cesium, but many precautionary measurements can be taken to prevent this. It is not very likely that people experience health effects that can be related to Cesium itself. When contact with radioactive Cesium occurs which is highly unlikely, a person can experience cell damage due to radiation of the Cesium particles. Due to this, effects such as nausea, vomiting, diarrhea and bleeding may occur. When the exposure lasts a long time people may even lose consciousness. Coma or even death may then follow .How serious the effects are depends upon the resistance of individual persons and the concentration a person is exposed to. Cesium in air can travel long distances before settling on earth .In water and soil most Cesium compounds are very water soluble. In soils, however, Cesium does not rinse out into the groundwater. It remains within the top layers of soils as it strongly bonds to soil particles and as a result it is not readily available for uptake through

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plant roots. Radioactive Cesium does have a chance of entering plants by falling on leaves. (Qygaard and Gjengedal, 2009, Silva *et al.*, 2009). Probably the most widespread use of Cesium today is in Cesium form based drilling fluids for the oil industry. Cesium is also used in atomic clocks, which are accurate to seconds in many thousands of years. ^{134}Cs has been used in hydrology as a measure of Cesium output by the nuclear power industry. Like other elements of group I Cesium has a great affinity for oxygen and is used as "getter" in vacuum tubes. Cesium is used as a catalyst in the hydrogenation of certain organic compounds. Radioactive isotopes of Cesium are used in medical field to treat certain types of cancer. ^{137}Cs is a common radioisotope used as a gamma emitter in industrial applications such as, moisture density gauge, leveling gauges, thickness gauges. Because of widespread application of Cesium in different fields of industry and medicine, determination of Cesium in real samples is of great importance. In this work we have developed a new Cesium ion-selective electrode based on parent Calix[4]arene for potentiometric determination of Cesium in real samples. (Rui-Fang *et al.*, 2007, Creavena *et al.*, 2009, Adhikari and Majumdar, 2004, Bereczki *et al.*, 2006). Calixarenes are synthetic macro cycles obtained by condensation of p-substituted phenol and formaldehyde in alkaline medium. Lower and upper rim functionalization of parent calixarenes led to a large variety of derivatives. Their bowl-like structure allows them to form complexes with a variety of species (Fig. 1).

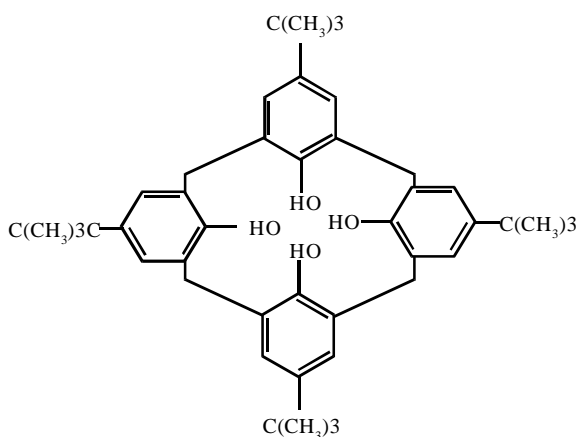


Fig. 1. Structure of THC

There are quite a number of reports in literature on Cesium ion-selective electrodes based on ion-exchangers, tetra phenyl borate and its derivatives (Arvand-Barmchi *et al.*, 2002; Attiyat *et al.*, 1988) TMC-crown, formazane (Baumann, 1976), crowned benzoquinones (Eisenman and Rudin, 1957), crownethers (Fallon *et al.*, 1996; Fung *et al.*, 1980, kimaura *et*

al., 1979; Meier *et al.*, 1984), acetonitrile derivatives (Saleh, 1998), Cesium-molybdophosphate (Arida *et al.*, 2004), derivative of γ -pyrone (Ashassi-Sorkhabi, *et al.*, 2001), lipophilic tetraesters of calix[6]arene and calix[6]diquinone (Oh *et al.*, 2000), calix[4] crownether-ester (Mahajan *et al.*, 2002), calix[4]arene-bis(crown-6-ether), (Vincent *et al.*, 2006) and calyx[4] arene dibenzocrown ethers (Kim *et al.*, 1999). In this work we used parent Calix[4]arene (THC) as ionophore in a pvc based Cesium ion-selective electrode.

MATERIALS & METHODS

p-5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrahydroxy calix[4]arene (THC) as ionophore from Aldrich and used without further purification. Acetophenone (AP), Benzyl Acetate (BA), Dibutylphthalate (DBP), Tetra Hydro Furan (THF), Oleic Acid (OA), Sodium Tetra-Phenyl Borate (NaTPB) from Merck, O-NitroPhenyl octyl ether (O-NPOE) and high molecular weight Poly Vinyl Chloride (PVC) purchased from Fluka. Nitrate salts of metal ions were all Merck analytical-reagent grade. All solutions and standards were made up in double distilled water. The PVC membranes were prepared according to the following general procedure. Amounts of membrane ingredients (membrane number 8 in Table.1) were mixed and dissolved in 2 ml THF and the mixture was transformed into a glass dish of 2 cm diameter. The solvent was evaporated slowly and an oily concentrated mixture was obtained. A Pyrex tube with 5mm internal diameter was dipped into the mixture for about 10 seconds and a semi-transparent membrane of about 0.3-0.5mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 12 hours, until it was completely dry and hard. The tube was then filled with 1×10^{-3} M Cesium nitrate as internal filling solution. The electrode was finally conditioned for 48 hours. A silver/silver chloride electrode was used as internal reference electrode. All potential measurements were carried out with the following cell assembly:

Ag/AgCl | cesium ion internal solution | pvc membrane | Test solution || SCE

Potentiometric selectivity coefficients for Cesium ion-selective electrode relative to other alkali and alkaline earth, ammonium and some transition metal ions were determined by Matched Potential Method (MPM) Table. 2. This method does not depend on the Nicolsky-Eisenman equation at all (Umezawa *et al.*, 2000, Nicolsky 1937, Bakker, 1996). In this method, the potentiometric selectivity coefficient is defined as the activity ratio of primary and interfering ions that give

Table 1. Optimization of membrane ingredients of Cs⁺-selective electrode

NO.	%PVC	%THC	%NPOE	%DBP	%AP	%OA	%NaTPB	Slope(mv/decade)
1	33.33	0.66	65.82	--	--	0.18	--	--
2	30	3	47	--	--	5	--	--
3	30	1.3	71	--	--	--	--	--
4	30	--	68	--	--	2	--	--
5	30	--	48	--	--	3.2	--	--
6	30	7	60.5	--	--	--	2	36
7	30	7	--	60.5	--	--	2	50
8*	30	8	--	59	--	--	3	58.5
9	30	--	--	67	--	--	3	va
10	30	8	--	62	--	--	--	54
11	30	8	--	60	--	--	2	57
12	30	6.8	--	52.2	--	--	11	va
13	30	8	--	--	59	--	3	11.2
14	30	8	--	57	--	--	5	54
15	29	7.8	--	--	56	7.2	--	--

the same potential change under identical conditions. At first, a known activity (a'_A) of the primary ion solution is added into a reference solution that contains a fixed activity (a_A) of primary ions, and the corresponding potential change (ΔE) is recorded. Next, a solution of an interfering ion is added to the reference solution until the same potential change (ΔE) is recorded. The change in potential produced at the constant background of the primary ion must be the same in both cases (Pungor, 1998).

Pot KA, B = (a'A-aA)/aB

RESULTS & DISCUSION

Cesium selective electrode was prepared by incorporating THC as ionophore in PVC membrane plasticized with DBP as the best membrane solvent as shown in (Fig. 2). According to Table 1, membrane No.8 showed the best sensitivity and linear range for the potential response of the Cesium electrode. The calibration plot of E (mv) vs.-log [Cs+], showed a Nernstian response(Fig. 3) with an average slope of 58.5 ± 0.6 mv per decade over a concentration range of $.1 \times 10^{-1} - 3.16 \times 10^{-5}$ M with a detection limit of 1.58×10^{-5} M. Dynamic response of the electrode with ten fold changes of Cesium concentration was studied

Table 2. Selectivity coefficient of Cs⁺ with respect to some interfering cations

M ⁿ⁺	LogK _{A,B}
H ⁺	-2.25
NH ₄ ⁺	-2.32
Rb ⁺	-2.4
Mg ²⁺	-4.0
Mn ²⁺	-3.9
Pb ²⁺	-3.1
Co ²⁺	-3.68
Al ³⁺	-3.93
Na ⁺	-3.15
K ⁺	-2.63
Ni ²⁺	-3.87
Ca ²⁺	-3.98
Cu ²⁺	-3.0
Fe ³⁺	-3.03
Cr ³⁺	-3.8
Ba ²⁺	-3.28

and a good response time of about 10 seconds was observed (Fig. 4). The life time of electrode was about 6 weeks and reproducible results were observed during this time. To show the stability and reproducibility of the electrode response, replicate measurements were done on a single solution of 1×10^{-3} M Cesium nitrate in 30 minutes intervals and a standard deviation of ± 0.6 mv was achieved. The effect of pH on the potential response of the electrode is shown in (Fig.5).The optimum pH range is 5.0 to 8.5. The results are summarized in Table 3.

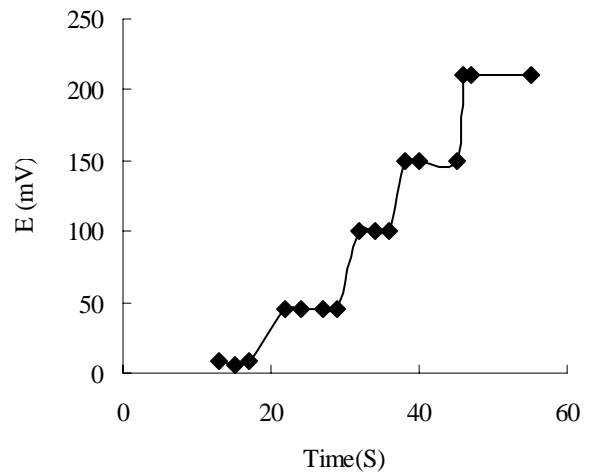


Fig. 4. Dynamic response of the electrode for ten-fold increase in Cesium concentration

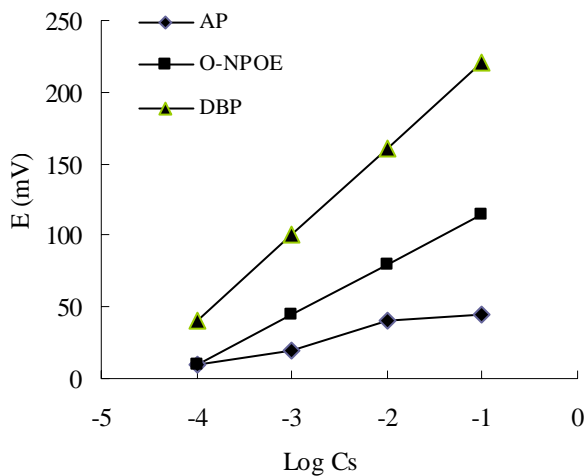


Fig. 2. Effect of different plasticizers on electrode response

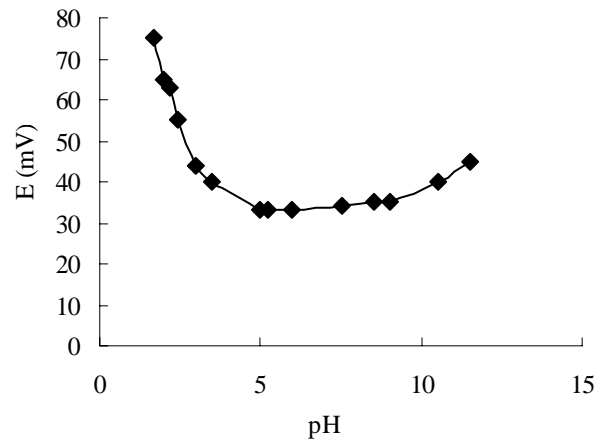


Fig. 5. Effect of pH on electrode response

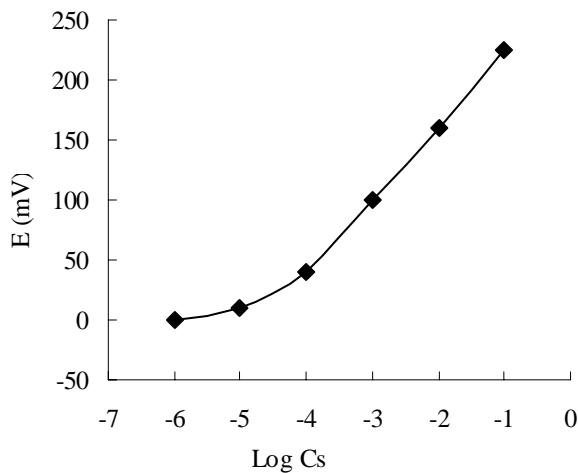


Fig. 3. Calibration curve for Cesium ion-selective electrode

Table 3. determination of Cs⁺ ion in spiked river water

determinations	added	found	Recovery
3	0.0	ND	0.0
3	1×10^{-4} M	9.9×10^{-5}	99 % (2%) *
3	1×10^{-3} M	1.02×10^{-3}	102 % (1.5%) *
3	1×10^{-2}	9.7×10^{-3}	97 % (2.5%) *

*numbers in parenthesis are RSD%

CONCLUSION

The optimized Cesium-selective electrode lends itself quite well for determination of Cesium in real samples. To assess the applicability of the electrode to real samples, it was used to test the recovery of

Cesium ion from tap water. A new cesium ion selective PVC membrane based on parent calix [4] arene was developed for potentiometric determination of cesium in environmental samples. The electrode based on p-5,11,17,23tetra(tert-butyl)25,26,27,28-tetrahydroxy calix[4]arene(THC) as ionophore, dibutyl phthalate (DBP) as plasticizer, sodium tetra phenyl borate(NaTPB) and oleic acid as lipophilic salt and additive showed the best performance.

REFERENCES

- Abdullahi, M. S., Uzairu, A. and Okunola, O. J. (2009). Quantitative Determination of Heavy Metal Concentrations in Onion Leaves, *Int. J. Environ. Res.*, **3** (2), 271-274.
- Adhikari, B. and Majumdar, S. (2004). Polymers in sensor applications *Prog. Polym. Sci.*, **29**, 699-766.
- Ahmad, M. K., Islam, S., Rahman, S., Haque, M. R. and Islam, M. M. (2010). Heavy Metals in Water, Sediment and Some Fishes of Buriganga River, Bangladesh. *Int. J. Environ. Res.*, **4** (2), 321-332.
- Arida, H. A. M., Aglan, R. F. and El-Reefy, S. A. (2004). A New Cesium Ion Selective Graphite Rod Electrode Based on Cs-molybdophosphate. *Analytical Letters*, **37**, 21-23.
- Arvand-Barmchi, M. and Mousavi, M. F. (2002). Cesium-selective poly (vinyl chloride) membrane electrode based on a new Calix [4] arene derivatives. *Analytical Letters*, **35** (5), 767-783.
- Ashassi-Sorkhabi, H., Rostamikia, T. and Shahriza, A. (2001). Cesium-ion selective electrode based on pyrone compound, *Bulletin of electrochemistry*, **17**, 545-548.
- Attiyat, A. S. and Ibrahim, Y. A. (1988). Potentiometric selectivity study of TMC-Crown Formazan Ionophore for Cesium. *Microchem. J.*, **37**, 122.
- Baghvand, A., Nasrabadi T., Nabi Bidhendi G. R., Vosoogh, A., Karbassi A. R. and Mehrdadi N. (2010). Groundwater quality degradation of an aquifer in Iran central desert. *Desalination*, **260** (1-3), 264-275.
- Bakker, E., (1996). selectivity of liquid membrane ion-selective electrodes, *Electroanalysis*, **9** (1), 7-12.
- Berezcki, R., Csokai, V., Grun, A., Bitter, I. and Toth, K. (2006) Crown bridged thiocalix[4]arenes as cesium-selective ionophores in solvent polymeric membrane electrodes *Analytica Chimica Acta*, **569**, 42-49.
- Baumann, E. W. (1976). Determination of parts-per-million Cesium in simulated nuclear waste with the Cesium-selective electrode. *Anal. Chem.*, **48**, 548-552.
- Chibunda R. T., Pereka A. E., Phiri E. C. J. and Tungaraza, C. (2010). Ecotoxicity of Mercury Contaminated Sediment Collected from Mabubi River (Geita district, Tanzania) to the Early Life Stages of African Catfish (*Clarias gariepinus*), *Int. J. Environ. Res.*, **4** (1), 49-56.
- Creavena, B. S., Donlona, D. F. and McGinley, J. (2009). Coordination chemistry of calix[4]arene derivatives with lower rim functionalisation and their applications. *Coordination Chemistry Reviews*, **253**, 893-962.
- Dhir, B. and Kumar, R. (2010). Adsorption of Heavy Metals by *Salvinia* Biomass and Agricultural Residues, *Int. J. Environ. Res.*, **4** (3), 427-432.
- Eisenman, G. and Rudin, D. O. (1957). plastic membrane sensors from a disposed combined glass electrode. *Science*, **126**, 831-834.
- Fallon, M. G. and Molcahy, D. (1996). Cesium ion-selective electrodes based on crowned benzoquinones. *Analyst*, **121**, 127-131.
- Fung, K. W. and Wong, K. H. (1980). Cesium-selective chemically modified field effect transistors with calyx[4]arene-crown-6 derivatives. *J. Electroanal. Chem.*, **111**, 359.
- Karbassi, A. R., Nouri, J. and Ayaz, G. O. (2007). Flocculation of Trace Metals During Mixing of Talar River Water with Caspian Seawater *Int. J. Environ. Res.*, **1** (1), 66-73.
- Kim, J. S., Ohki, A., Ueki, R., Ishizuka, T., Shimotashiro, T. and Maeda, S. (1999). Cesium-ion selective electrodes based on calix[4]arene dibenzocrown ethers. *Talanta*, **48**, 705-710.
- Kimura, K. and Maeda, T. (1979). Cesium-selective pvc[poly(vinyl chloride) membrane electrode based on bis(crown ethers). *J. Electroanal. Interfacial Electrochem.*, **105**, 335-340.
- Lee, J. N. and Mohamed, C. A. R. (2009) Trace Metal Contents in the Porites Corals of Peninsular Malaysia *Int. J. Environ. Res.*, **3** (1), 85-94.
- Mahajan, R. K., Kumar, M. Sharma, V. and Kaur, I. (2002). Cesium ion selective electrode based on calix[4]crown ether-ester. *Talanta*, **58**, 445-450.
- Meier, P. C. and Morf, W. E. (1984). the principles of ion-selective electrodes. *Anal. Chim., Acta*, **1**, 156.
- Nasrabadi T., Nabi Bidhendi G. R., Karbassi A. R. and Mehrdadi N. (2010). Partitioning of metals in sediments of the Haraz River (Southern Caspian Sea basin). *Environmental Earth Sciences*, **59**, 1111-1117.
- Nasrabadi T., Nabi Bidhendi G. R., Karbassi A. R., Hoveidi H., Nasrabadi I., Pezeshk H. and Rashidinejad F. (2009). Influence of Sungun copper mine on groundwater quality, NW Iran. *Environmental Geology*, **58**, 693-700.
- Nicolosky, B. P. (1937). selectivity of potentiometric ion sensors *Zh.Fiz.Khim.* **10**, 495.
- Oh, H., Choi, E. M., Jeong, H., Nam K. C. and Jeon, S. (2000). Polyvinyl chloride membrane Cesium ion-selective electrodes based on lipophilic calyx[6]arene tetraester derivatives. *Talanta*, **53**, 535-542.
- Pungor, E., (1998). how to understand the response mechanism of ion selective electrodes. *Talanta*, **44** (9), 1505-1508.

Øygard, J. K. and Gjengedal, E. (2009). Uranium in Municipal Solid Waste Landfill Leachate. *Int. J. Environ. Res.*, **3** (1), 61-68.

Rui-Fang, C. Man-Cheng, H. Li-Hua, J. Shu-Ni, L. Yu-Cheng, J. and Shu-Ping, X. (2007). Activity coefficients of rubidium chloride and cesium chloride in methanol–water mixtures and a comparative study of Pitzer and Pitzer–Simonson–Clegg models (298.15 K), *Fluid Phase Equilibria*, **251**, 137-144.

Saleh, M. B. (1997). new cesiumion-selective electrode based on aniline-(1,3-dioxo-2-indanylidene) acetonitrile derivatives. *Talanta*, **46**, 885-895.

Silva, A. M., Nogueira, D. P., Ikematsu, P., Silveira, F. M., Bomback, M., Alves, S. H. Paula, F. P. and Camargo, P. B. (2009). Carbon Stocks and Isotopic Composition of the Organic Matter in Soils Covered by Native Vegetation and Pasture in Sorocaba, SP, Brazil. *Int. J. Environ. Res.*, **3** (3), 435-440.

Souchon, V., Leray, I. and Valeur, B. (2006). Selective detection of Cesium by a water-soluble fluorescent molecular sensor based on a calyx[4]arene-bis (crown-6-ether). *chem. Commun.*, **40**, 4224-4226.

Taghinia Hejabi, A., Basavarajappa, H. T. and Qaid Saeed, A. M. (2010). Heavy Metal Pollution in Kabini River Sediments, *Int. J. Environ. Res.*, **4** (4), 629-636.

Umezawa, Y., Buhlmann, P., Umezawa, K., Tohda, K. and Amemiya, S. (2000). Potentiometric selectivity coefficients of ion-selective electrodes. *Pure Appl. Chem.*, **72** (10), 1851-2082.