

Full Paper

An Ion-selective Electrode for Anion Perchlorate in Thick-film Technology

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Abstract: The ionophore 1,4,7,10,13-penta(*n*-octyl)-1,4,7,10,13-pentaazacyclopentadecane (L^1) was used for the development of miniaturised perchlorate-selective electrodes in thick-film technology. Different PVC membranes containing L^1 and the plasticizers *o*-nitrophenyl octyl ether (NPOE), dibutyl phthalate (DBP), bis(2-ethylhexyl)sebacate (DOS) and dibutyl sebacate (DBS) were prepared and placed on a graphite working electrode manufactured by using thick film serigraphic technology. The perchlorate selective electrode containing DBS as plasticizer showed a potentiometric Nernstian response of -57 mV per decade in a range of perchlorate concentration from 1×10^{-4} to 1×10^{-1} M with a detection limit of 5×10^{-5} M. The ion selective electrodes containing DBP and NPOE as plasticizers exhibit a working range from 6.3×10^{-5} to 1×10^{-1} M and 7.4×10^{-5} to 1×10^{-1} M for perchlorate, respectively, with a detection limit of ca. 2.2×10^{-5} M. For all three electrodes a response time of ca. 5 s was found. The prepared electrodes do not show appreciable decay of the slope for at least 25 days. Potentiometric selectivity coefficients ($\log K^{pot}_{ClO_4^-, X^-}$) with respect to the primary anion perchlorate were evaluated using the fixed interference method. These coefficients are of the order of $10^{-1.7}$ or smaller, indicating the relatively poor interference of the different anions studied.

Keywords: ion-selective electrodes, perchlorate, thick-film.

1. Introduction

Ion-Selective Electrodes (ISEs) have been widely used for more than thirty years in a wide range of applications for determining the concentration of certain ions in aqueous solution [1]. Among different fields of application of ISEs, we are especially interested in the development of ion-selective electrodes for anionic species [2-7]. Anions play fundamental roles in a wide number of environmental and biological processes and due to their importance the development of anion sensors and chemosensors has grown in importance in recent years and has become an important sub-area within the field of anion chemistry [8-11]. Anions show a wide range of shapes and geometries and a lot of them are pH-sensitive, factors that have to be taken into account when designing a specific anion host. Anion receptors thus use binding forces that typically involve hydrogen bonding, electrostatic interactions and coordination to suitable metal centres [12]. In this context, perhaps the most widely used scaffoldings for anion receptors are polyamines [13]. They are partially protonated in aqueous environments and usually display electrostatic and/or hydrogen bonding interactions with anionic chemical species. Despite this, there are a relatively low number of ion-selective electrodes containing polyamines as ionophores [14-15]. These are usually of the conventional PVC-membrane type, containing an ion-selective membrane attached to the end of a tube that contains an internal liquid reference solution and a reference electrode. An alternative to this system is the use of all solid state PVC electrodes in which the membrane is directly in contact with a conducting surface connected to the millivolt measuring device. One advantage of the latter approach is the lack of an internal standard solution, which leads to the potential development of miniaturised ion-selective electrodes. Among the different technologies that can be used for the fabrication of solid state PVC electrodes we are especially interested in thick film technology [16-18]. This technology has found an important application in electrochemical sensors and biosensors, as it offers a number of advantages such as simple construction, large-scale production and low cost.

As part of our investigation of the development of ion selective sensors for anions, we report here the design and development of a miniaturised perchlorate ion selective electrode using thick-film technology incorporating a PVC membrane containing a polyazacycloalkane as selective ionophore.

2. Experimental Section

2.1. Reagents.

Reagents grade o-nitrophenyl octyl ether (NPOE), dibutyl phthalate (DBP), bis(2-ethylhexyl)sebacate (DOS) and dibutyl sebacate (DBS), tetrahydrofuran (THF) and high molecular weight poly(vinylchloride) powder (PVC) were supplied by Aldrich. Perchlorate, thiocyanate, carbonate, nitrate, bromide, chloride, iodide, acetate, oxalate, sulfate and phosphate solutions were prepared from sodium or potassium salts and were obtained from Panreac. All the aqueous solutions were prepared with de-ionised distilled water (Milli-Q water purification system). The ionophore 1,4,7,10,13-penta(n-octyl)-1,4,7,10,13-pentaazacyclopentadecane was synthesised following literature procedures [4].

2.2. Materials and electrode preparation.

The perchlorate sensor consists of a thick film ion-selective electrode and a commercial reference Ag/AgCl electrode. For the working electrode the manufacturing technology was based on serigraphic technology on thick film. The screen printed process consists of forcing pastes of different characteristics over a substrate through screens using scrapers. Openings in the screen define the motif that will be printed on the substrate by serigraphy. The final thickness of the pastes can be adjusted by varying the thickness of the screens. The production of the electrodes was based on alumina substrate RUBALIT 708S (CeramTec, UK) of 2 in. x 2 in. x 0.635 mm pre-cut in 12 units of 0.5 in. x 0.66 in. In order to build the above indicated electrode, three screens were made, corresponding to three defined layers: namely, the conductive layer working as a conductor of the signal, the active layer working as active surface and the upper protection layer. A drop of the PVC membrane, containing the corresponding plasticizer and the ionophore dissolved in THF, was deposited on the surface of the active layer and allowed to dry.

The conductive paste used was Ag/Pd/Pt C4081T (supplied by HERAEUS). The layout of the tracks was made to join the board to a flat cable connector with a separation of 3 mm between terminals. The active C paste was supplied by GEM. The protective paste was the 240-SB model supplied by ESL. The thick-film electrodes were made using serigraphic methods, using polyester screens with a density of 230 mesh (Saatilane Hitech 90/48 supplied by Saatile) and films of 50 μm thickness (Ulano CDF5 supplied by Ulano). The pastes were applied by a semiautomatic serigraphic machine (AUREL model C1010). A final thickness of 30 μm after firing was achieved. The conductive paste firing process was carried out at 850 °C in a cycle of 60 min with a peak of 10 min. A similar cycle, but with heating at 150 °C in a cycle of 60 min, was used to prepare the C active surface. The firing process of the protective paste was carried out at a temperature of 150 °C in a cycle of 60 min.

2.3. Measurements.

Measurements were carried out using the operational amplifier OPA129P with high input impedance ($10^{15} \Omega$) in buffer configuration and an active pass-bass filter to avoid interference from the electrical network. An acquisition card ADLINK, model PCI9112 inserted into a personal computer. A program developed with VEE-Pro software was used to acquire the data. The resolution in measure acquisition was ± 0.61 mV. Potentiometric measurements were performed with a two-electrode system where the working electrode was the thick film ion-selective electrode and the reference electrode was an Ag/AgCl electrode with 3M internal KCl solution.

The detection limit was defined as the intersection of the extrapolated linear regions of the calibration graph. Potentiometric selectivity coefficients were determined according to the fixed interference method using a 0.1 M solution of the corresponding interfering ion [19-20]. Activity coefficients were calculated according to the Debye-Hückel approximation. Calibration curves were constructed by plotting the potential, E, vs the logarithm of the potassium perchlorate activity at pH 7.0. All the measurements were carried out at room temperature.

3. Results and Discussion

3.1. The emf response characteristics.

The source of perchlorates in water and the soil is mainly anthropogenic as a consequence of their use in a wide range of different applications. Thus for instance, perchlorate is used as an oxidant in solid propellant for rockets and missiles, in certain fireworks, in the manufacture of matches, in nuclear reactors and electronic tubes, in tanning and finishing leather, in electroplating, etc. The toxicity of perchlorate is an active area of research [21-22], mainly focussed on the potential of perchlorate to hamper the synthesis of thyroid hormones and the potential consequences. Accordingly, the need for analytical methods for the detection of perchlorate might be of interest, especially in situations where conventional techniques are not suitable, as is the case in many on-site analyses and rapid screening applications. In these fields, optical and electrochemical sensing devices play an important role, for instance using ion-selective electrodes.

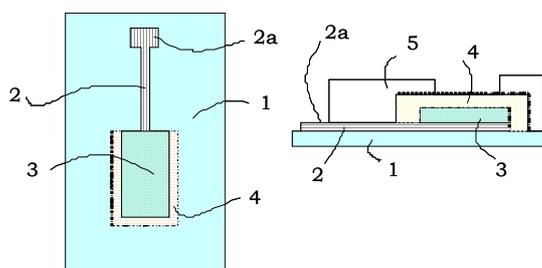
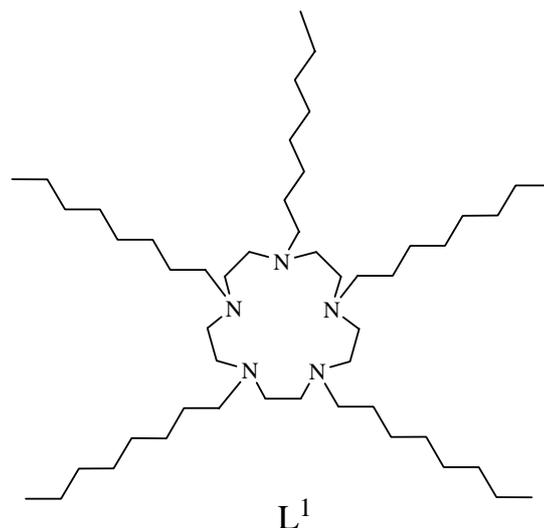


Figure 1. Schematic representation and transversal view of the electrode.

With these ideas in mind we approached the potential development of miniaturised perchlorate electrodes using thick-film technology. Figure 1 displays the scheme and transversal view of the potentiometric electrodes shown in this paper. They consist of (1) a substrate made of isolating material, (2) a layer of conductive material over the substrate, (2a) a terminal area as a part of the conductive material, (3) a layer of active material (graphite), (4) a layer of the PVC membrane containing the ionophore and (5) an insulating layer which covers the whole electrode except for the active and terminal areas. The synthesis of the ionophore used (1,4,7,10,13-penta(*n*-octyl)-1,4,7,10,13-pentaazacyclopentadecane, L^1 , (see Scheme 1)) was carried out following previously reported procedures [4]. The ion selective membranes were prepared by mixing in 5 ml of THF, the PVC, the plasticizer and the ionophore. The mixture was used to coat the graphite working electrode and the solvent was allowed to evaporate overnight. The final electrode was finally prepared for three days by soaking it in a 0.1 M potassium perchlorate solution-HEPES at pH 7. When not in use the electrode was kept immersed in the same solution. L^1 was introduced in the membrane in its unprotonated form, however the membrane made with L^1 gave a clear and stable response to perchlorate, suggesting that L^1 is finally protonated after the stabilisation of the membrane. This argument is based in the general idea that ISEs only function when a charge opposite to the charge of the analyte is present in the membrane.



Scheme 1. Structure of the ionophore 1,4,7,10,13-penta(n-octyl)-1,4,7,10,13-pentaazacyclopentadecane.

As is well-known the final response of ion-selective electrodes in relation to selectivity, stability, etc. depends not only on the ionophore, but also on the use of a certain plasticizer and in the proportion of the different membrane ingredients. Because of the number of these factors, in the first step several proportions of the membrane components (ionophore, plasticizer and PVC) were tested. Also, different membranes were prepared using four plasticizers; namely *o*-nitrophenyl octyl ether (NPOE), dibutyl phthalate (DBP), bis(2-ethylhexyl)sebacate (DOS) and dibutyl sebacate (DBS). Additionally, the membranes were prepared using different proportions of the ionophore in the 1 – 10 wt.% range. All the membranes set were tested against perchlorate and other anions. The best results in terms of stability and selectivity against perchlorate were observed when the membrane was prepared with a proportion of ca 2.8 wt.% of the ionophore and the final composition for the membranes was 2.8 wt % of ionophore, 56.0 wt % PVC and 41.2 wt % of the corresponding plasticizer. The different responses in terms of slope, detection limit and linear range of the prepared electrodes in relation to the use of different plasticizers are reported in Table 1.

Table 1 . Response characteristics of the different perchlorate-selective electrodes in thick-film technology.

ELECTRODE	L^1 – DBS	L^1 - DBP	L^1 - NPOE
Slope (mV per decade)	-57	-70.2	-70.3
Detection limit (mol l ⁻¹)	5×10^{-5}	2.2×10^{-5}	2.3×10^{-5}
Lineal range (mol l ⁻¹)	1×10^{-4} - 1×10^{-1}	6.3×10^{-5} - 1×10^{-1}	7.4×10^{-5} - 1×10^{-1}

The electrode containing DOS as plasticizer shows a very poor reproducibility and stability and was not studied. In contrast, the perchlorate selective electrode containing DBS as plasticizer showed a potentiometric Nernstian response of -57 mV per decade in a range of perchlorate concentration from 1×10^{-4} to 1×10^{-1} M with a detection limit of 5×10^{-5} M. The response of the electrode to perchlorate

and other inorganic anions is shown in Figure 2. The ion selective electrode containing DBP and NPOE as plasticizers exhibits a working range from 6.3×10^{-5} to 1×10^{-1} M and 7.4×10^{-5} to 1×10^{-1} M for perchlorate respectively with a detection limit of ca. 2.2×10^{-5} M. For all three electrodes a response time of ca. 5 s was found as the time required for the membrane electrode to reach a potential within ± 1 mV of the final equilibrium when the measurements were performed alternatively in 10^{-2} and 10^{-4} mol L^{-1} solutions of perchlorate. The prepared electrodes do not show appreciable decay of the slope for at least 25 days. After this period of time it was quite common to observe loss of adherence of the membrane to the alumina and graphite support.

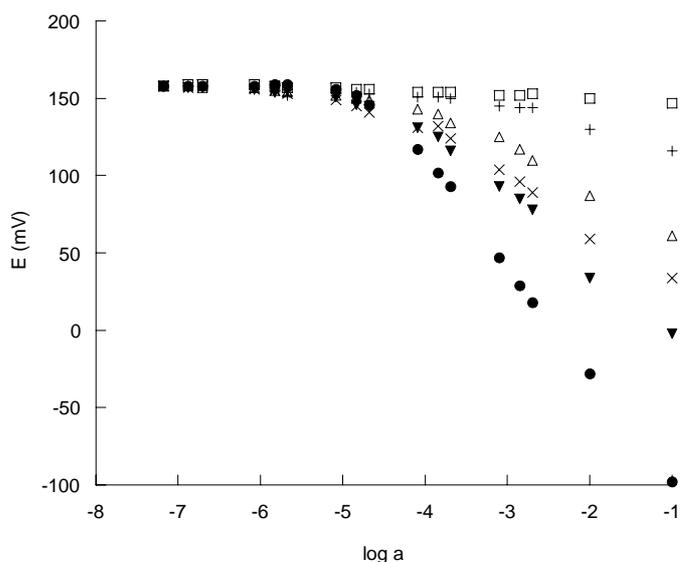


Figure 2. Potentiometric anion response to perchlorate (●) of the electrode L^1 containing DBP as plasticizer at pH 7 in the presence of certain anions, (▼) thiocyanate, (X) bromide, (Δ) nitrate, (+) chloride, (□) sulfate.

3.2. The effect of pH.

The effect of pH on the response of the membranes containing L^1 was tested over the pH range of ca. 5-13 at a fixed concentration of perchlorate of 1×10^{-4} M. As an example of the general observed behaviour the Figure 3 shows the results for the membrane containing L^1 and DBP as plasticizer. The pH was adjusted by using HCl or KOH. As can be observed (see Figure 3), there is a slight variation of the potential as a function of pH over the pH range 5-9. In highly alkaline media the potential decreases more significantly probably due to de-protonation of the ligand or due to membrane response to OH^- . A very similar behaviour was observed for the membranes containing L^1 as ionophore with the plasticizers o-nitrophenyl octyl ether or dibutyl sebacate.

3.3. Selectivity.

Selectivity is one of the most important characteristic of a sensor, as it helps to determine whether a reliable measurement of a target analyte is possible in a certain sample. Selectivity can be measured in terms of potentiometric selectivity coefficients ($\log K^{\text{pot}}_{\text{ClO}_4^-, \text{X}^-}$) that evaluates the response of the electrode to the primary anion in the presence of a certain interfering chemical species. $\log K^{\text{pot}}_{\text{ClO}_4^-, \text{X}^-}$

were evaluated using the fixed interference method at a concentration of interfering anions of 1.0×10^{-2} M.

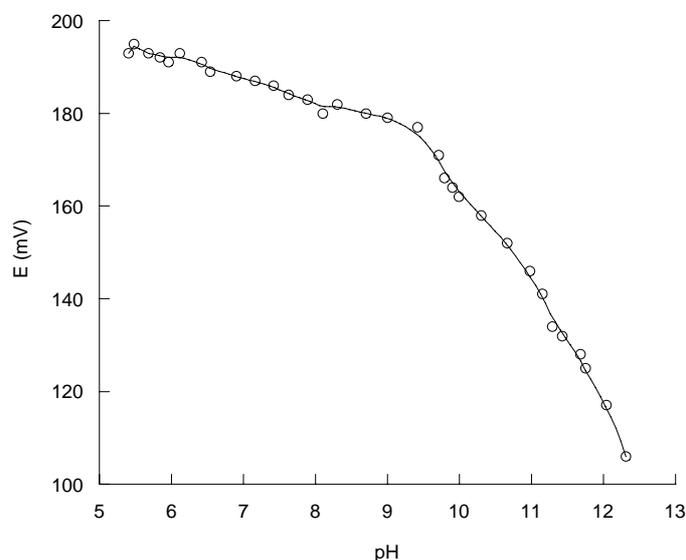


Figure 3. The pH effect on the potential of the membrane electrode containing L^1 , PVC and DBP.

Table 2. Potentiometric selectivity for perchlorate selective PVC membranes containing L^1 as ionophore and NPOE, DBP and DBS as plasticizers.

	L^1 - NPOE	L^1 - DBP	L^1 - DBS
Thiocyanate	-1.79	-1.93	-1.74
Carbonate	-3.03	-2.64	-1.78
Iodide	-2.19	-2.09	-2.10
Nitrate	-2.86	-2.66	-2.44
Bromide	-2.97	-2.80	-2.64
Acetate	-3.20	-3.00	-2.68
Chloride	-3.20	-3.00	-3.01
Phosphate	-3.74	-3.72	-3.16
Sulfate	-4.05	-4.10	-3.73
Oxalate	-4.12	-3.99	-3.79

Somewhat slightly better results in relation to the selectivity coefficients were obtained for the electrode containing L^1 and NPOE as plasticizer which exhibited a selectivity sequence of anion in the following order: $ClO_4^- > SCN^- > I^- > NO_3^- > Br^- > HCO_3^- > CH_3COO^- = Cl^- > phosphate > SO_4^{2-} > C_2O_4^{2-}$, whereas similar selectivity coefficients values were found for the membranes L^1 -DBP and L^1 -DBS. The selectivity sequence obtained for electrode L^1 -DBP was $ClO_4^- > SCN^- > I^- > HCO_3^- \cong NO_3^- > Br^- > CH_3COO^- \cong Cl^- > phosphate > C_2O_4^{2-} > SO_4^{2-}$, whereas that for L^1 -DBS was $ClO_4^- > SCN^- \cong HCO_3^- > I^- > NO_3^- > Br^- \cong CH_3COO^- > Cl^- > phosphate > SO_4^{2-} \cong C_2O_4^{2-}$. The selectivity sequences basically follows the Hofmeister Series ($ClO_4^- > SCN^- > I^- > NO_3^- > Br^- > Cl^- > HCO_3^- > CH_3COO^- > SO_4^{2-} > HPO_4^{2-}$) although some slight deviations might be interpreted on the basis of some preferential

coordination of the ionophore L^1 with certain anions. Table 2 and Figure 4 show the potentiometric selectivity coefficients for interfering anions relative to perchlorate for the electrodes L^1 -NPOE, L^1 -DBP and L^1 -DBS.

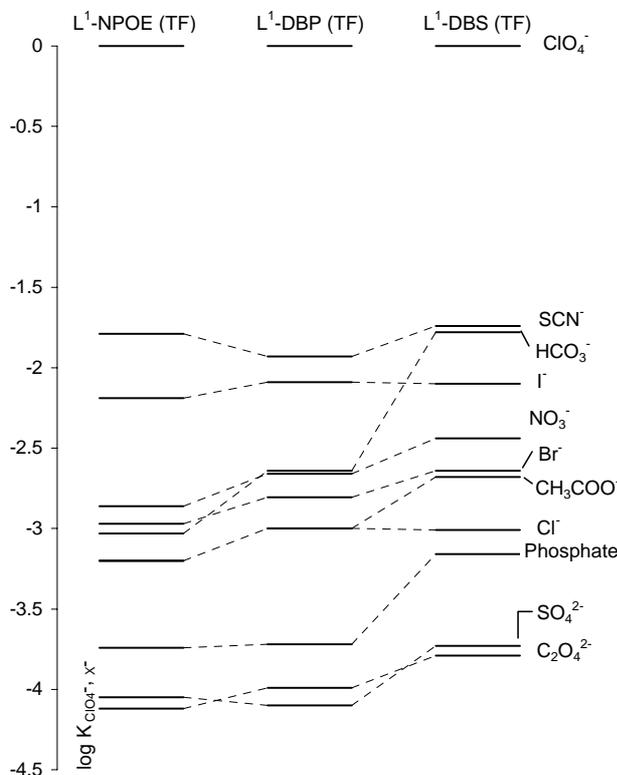


Figure 4. Potentiometric anion selectivity coefficients of electrodes containing the ionophore L^1 .

Since the development of the first perchlorate selective electrode [23-24] in 1969 a number of different perchlorate electrodes have been developed using both liquid membranes [25-30] and polymeric membranes [31-35]. Table 3 shows the response characteristics of some reported perchlorate-selective electrodes. As can be seen, the linear range and detection limit for the electrode we report here is on average slightly larger than those reported for similar perchlorate electrodes. However the detection limit of the thick-film electrode is still low enough for many applications. Additionally, if we take into account the selectivity coefficients, the prepared electrodes L^1 -NPOE, L^1 -DBP and L^1 -DBS displayed a quite selective response to perchlorate. Thus for instance, in these electrodes, the logarithm of the selectivity coefficients is lower than -2.5 for most of the tested anions (except for thiocyanate and iodide), indicating that these anions would not significantly interfere in the determination of perchlorate. In our case, if we compare the selectivity coefficients in Table 2, the best response is found for L^1 with the plasticizer NPOE (see Figure 4). These results compare well with those recently obtained by us using PVC membrane perchlorate-selective electrodes containing polyazacycloalkanes as carriers [4]. Besides the quite selective behaviour found in the use of polyamines as ionophores, in this case, we have the additional advantages of the potential for mass production and low-cost thick-film technology. In general the response found in terms of potentiometric selectivity coefficients for the three prepared electrodes, L^1 -NPOE, L^1 -DBP and L^1 -DBS is similar or lower than that reported when using a simple quaternary ammonium salt

(tetraoctylammonium chloride) as carrier [36-38], although the response is not as selective as that reported recently using a phosphadithia macrocycle [31] and a gold(I) complex [34].

Table 3. Characteristics of some reported perchlorate selective electrodes.

Ionophore	Electrode type	Linear range (M)	Detection limit (M)	Slope (mV decade ⁻¹)	Ref.
Phosphadithiamacrocycle	A	$1 \times 10^{-6} - 1 \times 10^{-2}$	8×10^{-7}	-56	31, 32
	B	$6 \times 10^{-7} - 1 \times 10^{-2}$	3×10^{-7}	-54	
Gold(I) complex	A	$5 \times 10^{-6} - 1 \times 10^{-2}$	1.1×10^{-6}	-56.8	35
Tetraphenylporphyrin	A	$8 \times 10^{-6} - 1.6 \times 10^{-1}$	5×10^{-6}	-57.8	36
	C	$1 \times 10^{-6} - 3 \times 10^{-2}$	7×10^{-7}	-53.6	
Tetraoctylammonium	A	8.2×10^{-6}	1.3×10^{-6}	-57.3	37
Tetraazamacrocycle	A	$1 \times 10^{-5} - 1 \times 10^{-1}$	5.6×10^{-6}	-55.0	4
Pentaazamacrocycle (L ¹)	A	$1 \times 10^{-5} - 1 \times 10^{-1}$	5.4×10^{-6}	-54.5	4
		$7.4 \times 10^{-5} - 1 \times 10^{-1}$	2.3×10^{-5}	-70.3	
Hexaazamacrocycle	A	$5.2 \times 10^{-6} - 1 \times 10^{-1}$	4.2×10^{-6}	-52.5	4
[Cu(tetraazamacrocycle)] ²⁺	A	$7.9 \times 10^{-5} - 1 \times 10^{-1}$	1.3×10^{-5}	-67.6	2

Ionophore: Phosphadithiamacrocycle, 7-phenyl-7-phospha-3,11-dithiabicyclo[11,4,0]heptadeca-13(1),14,16-triene(I). Gold(I) complex: bis[tri-(*p*-methoxyphenyl)phosphine]gold(I). Tetraazamacrocycle: 1,4,8,11-tetra(n-octyl)-1,4,8,11-tetraazacyclotetradecane. Pentaazamacrocycle: 1,4,7,10,13-penta(n-octyl)-1,4,7,10,13-pentaazacyclopentadecane. Hexaazamacrocycle: 1,4,7,10,13,16-hexa(n-octyl)-1,4,7,10,13,16-hexaazacyclooctadecane.

Electrode type: A, PVC membrane electrodes; B, membrane field-effects transistors; C, coated glassy carbon electrode; D, all solid state poly(vinyl chloride) membrane electrode.

Conclusions

In this work miniaturised PVC-membrane perchlorate-selective electrodes in thick-film technology were designed and developed. A selective response to perchlorate was found, with a fairly good detection limit, liner range and response time, Nernstian behaviour and relatively good potentiometric selectivity coefficients. We are currently developing new miniaturised electrodes for target anions using mass production and low-cost thick-film technology.

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References and Notes

1. Antonisse, M.M.G.; Reinhoudt, D.N. Potentiometric anion selective sensors. *Electroanalysis* **1999**, *11*, 1035-1048.
2. Seguí, M.-J.; Lizondo-Sabater, J.; Martínez-Máñez, R.; Sancenón, F.; Soto, J. A perchlorate-selective membrane electrode based on a Cu(II) complex of the ligand 1,4,8,11-tetra(n-octyl)-1,4,8,11-tetraazacyclotetradecane. *Analyst* **2002**, *127*, 387-390.
3. Lizondo-Sabater, J.; Martínez-Máñez, R.; Sancenón, F.; Seguí, M.-J.; Soto, J. Cobalt(II) and nickel(II) complexes of a cyclam derivative as carriers in iodide-selective electrodes. *Anal. Chim. Acta* **2002**, *459*, 229-234.
4. Lizondo-Sabater, J.; Seguí, M.-J.; Lloris, J.M.; Martínez-Máñez, R.; Pardo, T.; Sancenón, F.; Soto, J. New membrane perchlorate-selective electrodes containing polyazacycloalkanes as carriers. *Sens. Actuators B* **2004**, *101*, 20-27.
5. Seguí, M.-J.; Lizondo-Sabater, J.; Martínez-Máñez, R.; Pardo, T.; Sancenón, F.; Soto, J. Ion-selective electrodes for anionic surfactants using a new aza-oxa-cycloalkane as active ionophore. *Anal. Chim. Acta* **2004**, *525*, 83-90.
6. Coll, C.; Labrador, R.H.; Martínez-Máñez, R.; Soto, J.; Sancenón, F.; Seguí, M.-J.; Sánchez, E. Ionic liquids promote selective responses towards the highly hydrophilic anion sulfate in PVC membrane ion-selective electrodes. *Chem. Commun.* **2005**, 3033-3035.
7. Seguí, M.J.; Lizondo-Sabater, J.; Martínez-Máñez, R.; Sancenón, F.; Soto, J. Linear polyamines as carriers in thiocyanate-selective membrane electrodes. *Talanta* **2006**, *68*, 1182-1189.
8. Martínez-Máñez, R.; Sancenón, F. Fluorogenic and chromogenic chemosensors and reagents for anions. *Chem. Rev.* **2003**, *103*, 4419-4476.
9. Gupta, V.K.; Ludwig, R.; Agarwal, S. Anion recognition through modified calixarenes; a highly selective sensor for HPO_4^{2-} . *Anal. Chim. Acta* **2005**, *538*, 213.
10. Jain, A.K.; Gupta, V.K.; Singh, L.P.; Srivastava, P.; Raison, J.R.; Anion recognition through novel C-thiophenecalix[4]resorcinarene: PVC based sensor for chromate ions. *Talanta*, **2005**, *65*, 716-721.
11. Gupta, V.K.; Agarwal, S. PVC based 5,10,15,20-tetrakis (4-methoxyphenyl) porphyrinatocobalt(II) membrane potentiometric sensor for arsenite. *Talanta* **2005**, *65*, 730-734.
12. Beer, P.D.; Gale, P.A.; Anion recognition and sensing: the state of the art and future perspectives *Angew. Chem. Int. Ed.* **2001**, *40*, 486-516.
13. Descalzo, A.B.; Marcos, M.D.; Martínez-Máñez, R.; Soto, J.; Beltrán, D.; Amorós, P. Anthrylmethylamine functionalised mesoporous silica-based materials as hybrid fluorescent chemosensors for ATP. *J. Mater. Chem.* **2005**, *15*, 2721-2731.
14. Carey, C.M.; Riggan Jr., W.B. Cyclic polyamine ionophore for use in a dibasic phosphate-selective electrode. *Anal. Chem.* **1994**, *66*, 3587-3591.

15. Hartley, A.M.; House, W.A.; Callow, M.E.; Leadbeater, B.S.C. Application of a cyclic polyamine ionophore in phosphate selective electrodes for environmental analysis. *Int. J. Environ. Anal. Chem.* **2000**, *76*, 199-214.
16. Martínez-Máñez, R.; Soto, J.; Lizondo-Sabater, J.; García-Breijo, E.; Gil, L.; Ibáñez, J.; Alcaina, I.; Alvarez, S. New potentiometric dissolved oxygen sensors in thick film technology. *Sens. Actuators B* **2004**, *101*, 295-301.
17. Martínez-Máñez, R.; Soto, J.; García-Breijo, E.; Gil, L.; Ibáñez, J.; Llobet, E. An “electronic tongue” design for the qualitative analysis of natural waters. *Sens. Actuators B* **2005**, *104*, 302-307.
18. Martínez-Máñez, R.; Soto, J.; García-Breijo, E.; Gil, L.; Ibáñez, J.; Gadea, E. A multisensor in thick-film technology for water quality control. *Sens. Actuators A* **2005**, *120*, 589-595.
19. Bakker, E.; Bühlmann, P.; Pretsch, E. Carrier-based ion-selective electrodes and bulk optodes. *Chem. Rev.* **1997**, *97*, 3083-3132.
20. IUPAC, Selectivity coefficients for ion-selective electrodes: recommended methods for reporting $K_{A,B}^{POT}$ values. *Pure Appl. Chem.* **1995**, *67*, 507-518.
21. McNabb, F.M.A.; Jang, D.A.; Larsen, C.T. Does thyroid function in developing birds adapt to sustained ammonium perchlorate exposure?. *Toxicol Sci.* **2004**, *82*, 106-113.
22. Miranda, L.A.; Pisano, A.; Casco, V. Ultrastructural study on thyroid glands of *Bufo arenarum* larvae kept in potassium perchlorate solution. *Biocell.* **1996**, *20*, 147-153.
23. Ross, J.W. in *Ion Selective Electrodes*, ed. R.A. Durst, US Government Printing Office, Washington, DC, **1969**, p. 57.
24. Orion Research, *Br. Pat.*, 1197264, **1968**.
25. Rohm, T.J.; Guilbault, G.G. New methods for the preparation of perchlorate ion-selective electrodes. *Anal. Chem.* **1974**, *46*, 590-592.
26. Wilson, A.C.; Pool, K.H. An improved ion-selective electrode for perchlorate. *Talanta* **1976**, *23*, 387-388.
27. Hassan, S.S.M.; Elsaied, M.M. A new liquid membrane electrode for selective determination of perchlorate. *Talanta* **1986**, *33*, 679-684.
28. Jain, A.K.; Jahan, M.; Tyagi, V. Construction and assessment of some perchlorate-selective liquid membrana electrodes. *Anal. Chim. Acta* **1990**, *231*, 69-75.
29. Coetzee, C.J.; Freiser, H. Anion responsive electrodes based on ion-association extraction systems. *Anal. Chem.* **1968**, *40*, 2071-2071.
30. Coetzee, C.J.; Freiser, H. Liquid-liquid membrane electrodes based on ion association extraction systems. *Anal. Chem.* **1969**, *41*, 1128-1130.
31. Casabó, J.; Escriche, L.; Pérez-Jiménez, C.; Muñoz, J.A.; Teixidor, F.; Bausells, J.; Errachid, A. Application of a new phosphadithiamacrocycle to ClO_4^- selective CHEMFET and ion-selective devices. *Anal. Chim. Acta* **1996**, *320*, 63-68.
32. Errachid, A.; Pérez-Jiménez, C.; Casabó, J.; Escriche, L.; Muñoz, J.A.; Bratov, A.; Bausells, J. Perchlorate-selective MEMFETs and ISEs based on a new phosphadithiamacrocycle. *Sens. Actuators B* **1997**, *43*, 206-210.
33. Siswanta, D.; Takenaka, J.; Suzuki, T.; Sasakura, H.; Hisamoto, H.; Suzuki, K. Novel neutral anion ionophores based on fluorinated polyether compounds as a sensory molecule for ion-selective electrodes. *Chem. Lett.* **1997**, 195-196.

34. Sánchez-Pedreño, C.; Ortuño, J.A.; Hernández, J. Perchlorate-selective polymeric membrana electrode base don a gold(I) complex: application to water and urine análisis. *Anal. Chim. Acta* **2000**, *415*, 159-164.
35. Shamsipur, M.; Soleymanpour, A.; Akhond, M.; Sharghi, H.; Hasaninejad, A.R. Perchlorate selective membrane electrodes based on a phosphorus(V)-tetraphenylporphyrin complex. *Sens. Actuators B* **2003**, *89*, 9-14.
36. Pérez-Olmos, R.; Rios, A.; Martín, M.P.; Lapa, R.A.S.; Lima, J.L.F.C. Construction and evaluation of ion selective electrodes for perchlorate with a summing operational amplifier: application to pyrotechnic mixtures analysis. *Analyst* **1999**, *124*, 97-100.
37. Fogg, A.G.; Pathan, A.S.; Burns, D.T. A liquid-state perchlorate ion-selective electrode based on brilliant green perchlorate. *Anal. Chim. Acta* **1974**, *73*, 220-223.
38. Kataoka, M.; Kambara, T. A liquid membrane type perchlorate ion-selective electrode. *J. Electroanal. Chem.* **1976**, *73*, 279-284.

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