

Perchlorate selective membrane electrodes based on a platinum complex

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Abstract Three platinum(II) complexes were synthesized and studied to characterize their ability as an anion carrier in a PVC membrane electrode. The polymeric membrane electrodes (PME) and also coated glassy carbon electrodes (CGCE) prepared with one of these complexes showed excellent response characteristics to perchlorate ions. The electrodes exhibited *Nernstian* responses to ClO_4^- ions over a wide concentration range from 1.5×10^{-6} to 2.7×10^{-1} M for PME and 5.0×10^{-7} to 1.9×10^{-1} M for CGCE with low detection limits (9.0×10^{-7} M for PME and 4.0×10^{-7} M for CGCE). The electrodes possess fast response time, satisfactory reproducibility, appropriate lifetime and, most importantly, good selectivity toward ClO_4^- relative to a variety of other common anions. The potentiometric response of the electrodes is independent of the *pH* of the test solution in the *pH* range 2.0–9.0. The proposed sensors were used in potentiometric determination of perchlorate ions in mineral water and urine samples.

Keywords Ion selective electrode; Perchlorate determination; PVC membrane electrode; Platinum complex; Potentiometry.

Introduction

Perchlorate is considered as a new persistent inorganic contaminant because of its specific properties, such as high water solubility, mobility, and stability

[1]. Due to disposal of perchlorate salts that are used in solid propellants, explosives, electro-polishing of metals, and pyrotechnics, such as fireworks, gun powder, explosives, and highway flares, perchlorate anions may be found at high concentration (more than 1000 ppm) in surface and ground waters [2]. Perchlorate shows thyrostatic activity by inhibiting iodine uptake and may therefore hinder the ability of humans to produce hormones and regulate their activities. Moreover, perchlorate salts have been used to treat patients with hyperactive thyroid glands (*Graves' disease*) and to carry out diagnostic tests [3]. Thyroid gland tumors were spotted in rodent animals after exposure to high dose of perchlorate ions [4]. Health risks at lower doses are still not well understood and studies are being conducted in order to determine safe levels in drinking water. Based on these findings, the determination of perchlorate ions in different samples such as ground water, propellants, explosives, and urine is very important. Therefore, several different methods have been used for the determination of perchlorate ions [5–10]. However, most of these methods are either time-consuming or need expensive instruments and also well-controlled experimental conditions and, most importantly, suffer from various interferences of cationic or anionic species. Hence, major efforts have been made to develop more convenient direct methods for the quick, easy, and inexpensive assay of perchlorate ions in different samples. One technique as a routine monitoring device is potentiometric measurement *via* an ion-selective electrode (ISE). Ion-selective

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polymeric membrane electrodes incorporating ion carriers with unique characteristics, such as ease of preparation, fast response, low cost, nondestructive, unaffected by color or turbidity, wide linear range, relatively low detection limit, and especially reasonable selectivity, can be very suitable tools for determination of perchlorate ions in different samples.

During the last three decades, many efforts have been focused on the introduction perchlorate-selective electrodes. Most of these reported electrodes were polymeric liquid membranes based on ion exchangers, where the electroactive species including perchlorate ion-association complexes with cations and different metal chelates [11–13], long chain quaternary ammonium ions [14–16], and organic dyes [17, 18] have been dissolved in various organic solvents. However, most of these electrodes are not sensitive and selective enough to permit selective measurement of low levels of perchlorate and also are susceptible to serious interferences from other common anions such as OH^- , NO_3^- , SCN^- , ClO_3^- , and I^- . Thus, in the past decade, there has been a growing interest to search suitable ionophores to construct carrier-based perchlorate selective electrodes with improved selectivity and sensitivity [19–24]. These reported electrodes were based on coordinative ionophores that showed to some extent selectivity and sensitivity. But, some of these electrodes still possess various limitations such as narrow concentration range, inadequate response time, and poor reproducibility. Thus, it is still desirable to continue efforts to construct perchlorate-selective electrodes with wider concentration range and lower detection limit. The aim of this paper is to develop new polymeric membrane (PME) and coated glassy carbon (CGCE) perchlorate ion-selective electrodes (ISEs) based on synthesized platinum(II) complexes (Fig. 1), $[\text{PtX}_2(\text{dppm})]$ ($X = \text{Me}$, $p\text{-MeC}_6\text{H}_4$, and Cl ; $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$), as perchlorate ionophores for sensitive and selective determination of perchlorate ions in different samples.

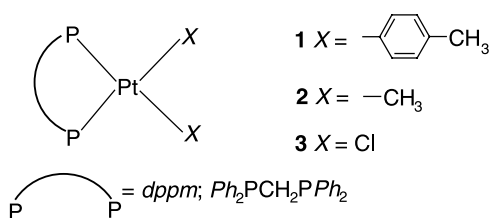


Fig. 1 Structure of platinum(II) complexes

Results and discussion

It is well known that metal-ion complexes in plasticized membrane electrodes can act as anion carriers which show potentiometric anion selectivity patterns different from the *Hofmeister* selectivity sequence. Thus, in this work, we were interested to investigate the possibility of using the synthesized platinum complexes (Fig. 1) as anion carriers in liquid membrane electrodes. Therefore, in preliminary experiments different membrane electrodes with these complexes were prepared [25, 26] and potentiometric responses of these electrodes to different anions were obtained. The electrode based on $[\text{Pt}(\text{MeC}_6\text{H}_4)_2(\text{dppm})]$ complex **1** showed excellent potential responses to ClO_4^- when compared to other anions tested. The potential responses of polymeric membrane electrodes (PME) containing different platinum complexes as a carrier to perchlorate ions are shown in Fig. 2. As can be seen from Fig. 2, under similar experimental conditions, the efficiency of platinum complex **1** as a ClO_4^- ion carrier in the membrane is better than for complexes **2** and **3**. Therefore, the complex **1** was selected for construction of a perchlorate selective electrode.

The potential responses of the PVC membrane electrode containing **1** to different anions, after conditioning in the potassium salt solution of each anion, in the concentration range 5.0×10^{-7} – $3.0 \times 10^{-2} \text{ M}$ are shown in Fig. 3. As seen, except for ClO_4^- , all other anions tested showed weak responses due to lower interaction with the ionophore in the membrane. We therefore studied in detail the properties of the electrode for perchlorate ions.

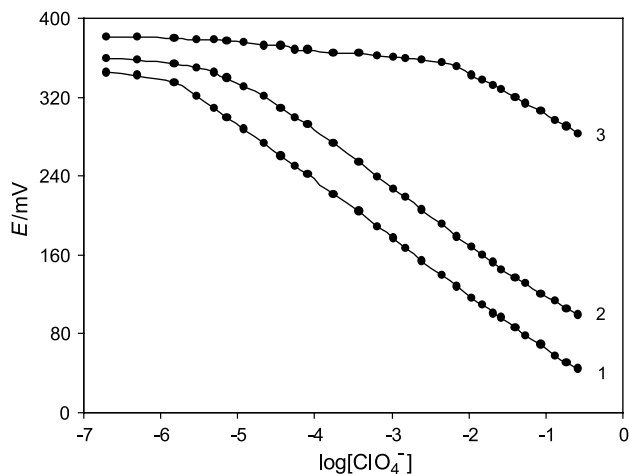


Fig. 2 Potential response of various platinum complexes to perchlorate ions: (1) **1**; (2) **2**; (3) **3**

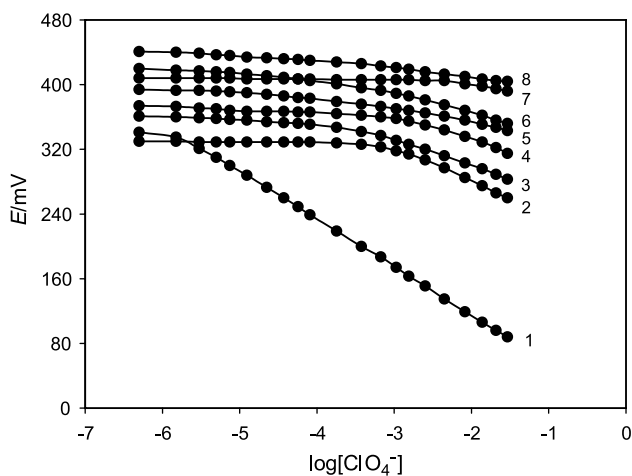


Fig. 3 Potential responses of an electrode based on complex **1** to various anions: (1) ClO_4^- ; (2) I^- ; (3) SCN^- ; (4) Br^- ; (5) NO_3^- ; (6) Cl^- ; (7) NO_2^- ; (8) SO_4^{2-}

In the case of ionophores based on different metal ion complexes [27–31], in addition to the electrostatic interaction between the central metal ion and analyte anion, there is a coordination action between both species involved. Thus, the selectivity sequence is dominated by both electrostatic and coordination forces and it is expected that both the nature of the central metal ion and the coordination ligand properties play important roles in determining the selectivity of the ionophore towards a specific anion. As seen, complex **1** shows more response to perchlorate ion than the other two platinum complexes **2** and **3**, more probably because of the existence of a paratolyl group in the coordination ligand. With the aid of UV/Vis spectra it is possible to show interaction between the platinum complex **1** and perchlorate ions. In acetonitrile, the complex ($1.0 \times 10^{-4} \text{ M}$) showed an absorption peak at 355.6 nm. The addition of an equimolar amount of sodium perchlorate to this solution resulted in a distinct increase in absorption. The substantial increase in the absorbance, after contact of the carrier solution with ClO_4^- ions, suggested that the absorbing species had increased in size and axial coordination might have taken place [32, 33]. Moreover, the influences of other anions on the spectrum of the platinum complex were also investigated, and almost no detectable spectral changes were observed.

The sensitivity, selectivity, and linearity of ion selective sensors not only depend on the nature of the ionophores used but also significantly on the membrane composition and the properties of the plasticiz-

Table 1 Optimization of membrane ingredients

No.	Composition (100 w)			Slope mV/decade	Linear range [ClO_4^-]/M
	PVC	Plasticizer	L1		
1	32.6	<i>NPOE</i> , 65.2	2.2	52.0	5.0×10^{-6} – 1.3×10^{-1}
2	32.5	<i>NPOE</i> , 64.9	2.6	59.5	1.5×10^{-6} – 2.7×10^{-1}
3	32.3	<i>NPOE</i> , 64.7	3.0	64.7	3.0×10^{-6} – 1.9×10^{-1}
4	32.5	<i>BA</i> , 64.9	2.6	49.2	7.5×10^{-6} – 1.3×10^{-1}
5	33.0	<i>NPOE</i> , 67.0	0.0	20.3	1.8×10^{-4} – 5.6×10^{-2}
6	32.5	<i>DOS</i> , 64.9	2.6	52.1	5.0×10^{-6} – 1.9×10^{-1}
7	32.5	<i>DBS</i> , 64.9	2.6	48.0	7.5×10^{-6} – 1.3×10^{-1}
8	32.5	<i>DBP</i> , 64.9	2.6	53.2	7.5×10^{-6} – 1.9×10^{-1}
9	32.5	<i>DMS</i> , 64.9	2.6	45.7	5.0×10^{-6} – 1.3×10^{-1}

ers used [34–38]. Thus, the effect of the membrane composition, the nature and amount of the plasticizer on the potential response of the ClO_4^- sensor were investigated and the results for PME are summarized in Table 1. As seen from Table 1, the key ingredient in the membrane is ionophore **1**. In fact, in the absence of the ionophore, the resulting membrane (No. 5) revealed a very limited slope and linear range due to the lipophilic characteristic of perchlorate anions. Since the nature of the plasticizer influences both the dielectric constant of the membrane phase and the mobility of the ionophore molecules, it was expected that the kind of plasticizer plays an important role in determining the ion selective electrode characteristics [36, 39]. Among six plasticizers examined, *NPOE* resulted in the best sensitivity and linear range. Moreover, 3.5% of the ionophore and a plasticizer/*PVC* ratio of 2 (No. 2) were chosen as the optimum amount in the *PVC* membrane. A further addition of ionophore (3.0%) however resulted in super-Nernstian slope with some decrease in linear range most probably due to some inhomogeneities of the membrane [40].

It has been clearly shown that in liquid membrane electrodes based on neutral carriers, the presence of lipophilic additives are necessary to introduce permselectivity, so that without such additives many electrodes fail to respond properly [36, 41]. However, the proposed electrode showed good response

characteristics to perchlorate anions without any additional additive. The *Nernstian* response of the proposed perchlorate-selective electrode in the absence of an additional lipophilic ion exchanger may be caused by possible trace impurities within the used *PVC* (and probably the carrier employed) [19, 20, 38, 40].

The influence of the concentration of the internal solution on the potential response of the ClO_4^- ion selective PME was studied. The NaClO_4 concentration was changed from 1.0×10^{-1} to 1.0×10^{-4} *M* and the potential response of the ClO_4^- ion selective PME was obtained. It was found that variation of the concentration of the internal solution did not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting *Nernstian* plot. A 1.0×10^{-3} *M* concentration of the internal reference solution was chosen because of the better correlation coefficient of the calibration plot ($R^2 = 0.997$).

Before use, the liquid membrane electrode must be conditioned by soaking in an anion solution in order to ensure the equilibrium at the membrane-water interface. Optimum conditioning time for the PME and CGCE in a 1.0×10^{-2} *M* sodium perchlorate solution was found to be 12 and 24 h. The conditioned electrodes then generated stable potentials when placed in contact with ClO_4^- solutions. The average time required for the membrane sensors to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of a series of perchlorate ion solutions, each having 10-fold difference in concentration, was less than 10 s over the entire concentration range and the potentials stayed constant after this time. The standard deviation of the potential responses over a period of 5 h in 1.0×10^{-3} *M* of ClO_4^- ions was 0.9 mV ($n = 30$), and the potential reading for the electrode dipped alternatively into stirred solutions of 1.0×10^{-3} and 1.0×10^{-4} *M* of ClO_4^- represented a standard deviation of 0.7 mV ($n = 6$).

The lifetime of an ion-selective electrode is usually defined as the time interval between the conditioning of the membrane and the moment when at least one of its response characteristics changes. The relative lifetime of the proposed perchlorate electrodes was studied by periodically recalibrating in a standard ClO_4^- solution and calculating the response slope over the range of 2.0×10^{-7} to 5.0×10^{-1} *M* NaClO_4 solutions. Before each measurement, the

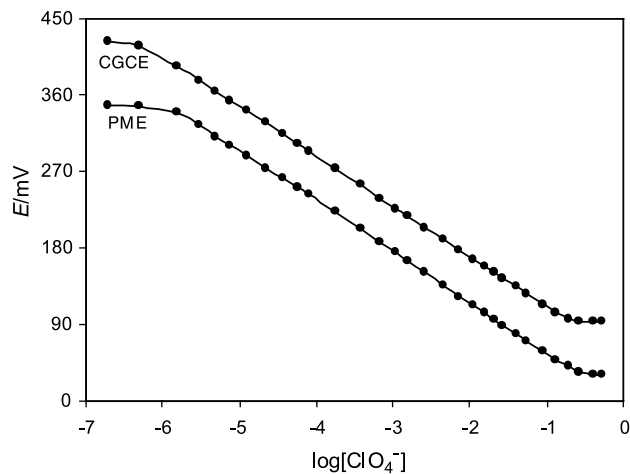


Fig. 4 Calibration graphs for the PME and CGCE

electrodes were conditioned in a 1.0×10^{-3} *M* sodium perchlorate. The experimental results showed that the lifetime of the ClO_4^- -selective electrodes were about 50 days. During this time the detection limit and slope of the electrodes remained almost constant.

The *emf* response of the proposed ClO_4^- selective electrodes based on platinum complex **1** (prepared under optimal membrane ingredients) at varying concentrations of perchlorate anions (Fig. 4) indicated a linear range from 1.5×10^{-6} to 2.7×10^{-1} *M* for PME and from 5.0×10^{-7} to 1.9×10^{-1} *M* for CGCE. The slopes of calibration curves were 59.5 ± 0.3 mV/decade ($n = 6$) for PME and 58.6 ± 0.4 mV/decade ($n = 6$) of ClO_4^- ion concentration for CGCE at 25°C. The limit of detection, according to the IUPAC recommendation of 1976, is defined by the cross section of the two extrapolated linear segments of calibration curves [42]. The limit of detection determined from the intersection of two extrapolated segment of the calibration graphs (Fig. 4), was 9.0×10^{-7} *M* and 4.0×10^{-7} *M* for the PME and CGCE.

The *pH* dependence of the potential response of the proposed membrane sensors at three different concentrations of ClO_4^- ions in the *pH* range of 1–10 was tested and the results are shown in Fig. 5. As can be seen, the electrode potential was independent of *pH* in the range 2.0–9.0. The observed potential drift at lower *pH* values is most probably due to the increase of the Cl^- ion concentration and simultaneous response of the electrode to perchlorate and chloride ions. While at higher *pH* values the drift could be due to the interference of OH^- ions on the complex formation between perchlorate ion and ionophore.

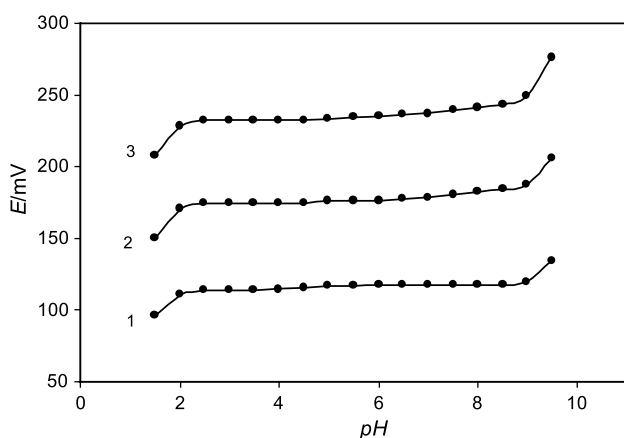


Fig. 5 Effect of pH of the test solution on the potential response of the perchlorate-selective electrode (PME) at three different ClO_4^- concentrations: (1) $1.0 \times 10^{-2} M$; (2) $1.0 \times 10^{-3} M$; (3) $1.0 \times 10^{-4} M$

Sometimes the samples may contain non-aqueous content, and so it is necessary the selective electrode also works well in such partially non-aqueous media. Thus, the performance of the proposed sensors was also investigated in partially non-aqueous media using methanol, ethanol, and acetone mixtures with water. The calibration plot of the electrode was obtained in different mixtures of methanol-water, ethanol-water, and acetone-water. From the data obtained (Table 2), it was concluded that the membrane electrodes worked satisfactorily in mixtures up to volume fractions $\varphi = 0.2$ non-aqueous content. In these mixtures the working concentration range and slope did not change reasonably, only a little decrease was observed. Therefore, the electrodes can be applied in solutions having up to 20% non-aqueous con-

Table 2 Effect of partially non-aqueous media on the response of ClO_4^- -selective polymeric membrane electrode (PME)

Non-aqueous content (100 φ)	Slope mV/decade	Linear range [ClO_4^-]/M
0	59.5	1.5×10^{-6} – 2.7×10^{-1}
Methanol		
10	58.9	3.0×10^{-6} – 2.7×10^{-1}
20	58.2	5.0×10^{-6} – 2.7×10^{-1}
Etanol		
10	58.7	5.0×10^{-6} – 2.7×10^{-1}
20	58.3	7.5×10^{-6} – 2.7×10^{-1}
Acetone		
10	58.1	5.0×10^{-6} – 2.7×10^{-1}
20	57.8	1.2×10^{-5} – 2.7×10^{-1}

tent. However, above 20% non-aqueous content, the slope and working concentration range were reduced, and the potentials showed drift probably due to leaching of the membrane ingredients and so caused a significant interference in electrode functioning.

The selectivity behavior is the most important characteristic of an ion selective electrode as it determines the applicability of any sensor in the presence of foreign ions in the samples. Selectivity interprets relative electrode response for the primary anion (A) over other anions present in solution (B), which is usually expressed in terms of potentiometric selectivity coefficient ($K_{A,B}^{\text{pot}}$). The potentiometric selectivity coefficients were determined by the fixed interference method (FIM) [43, 44] at $5.0 \times 10^{-3} M$ concentration of the interfering species. The resulting selectivity coefficients obtained for the proposed ClO_4^- ion selective electrodes (PME and CGCE) are listed in Table 3. From the data given in Table 3, it is revealed that the proposed perchlorate sensors have good selectivity toward perchlorate anion with respect to anions such as chloride, bromide, and nitrate. So, the disturbance produced by these anions is negligible in the determination process of perchlorate ions in the presence of foreign anions. Moreover, a comparison between the selectivity coefficients for the PME and, specially, CGCE, with those previously reported for other ionophore based perchlorate ion-selective electrodes [19–24], revealed that the proposed electrode shows in most cases somewhat similar, in some cases even superior, selectivity behavior to the PVC membrane sensors prepared previously. However, the proposed electrode is superior in terms of concentration range,

Table 3 Potential selectivity coefficients of various interfering anions

Interfering anion	$\log(K_{A,B}^{\text{pot}})$	
	PME	CGCE
Br^-	–3.0	–3.7
NO_3^-	–3.4	–3.9
SO_4^{2-}	–3.9	–4.3
Cl^-	–3.5	–3.7
I^-	–1.6	–1.9
SCN^-	–2.3	–2.5
F^-	–3.5	–3.9
$\text{C}_2\text{O}_4^{2-}$	–2.9	–3.2
OAc^-	–2.8	–3.2
NO_2^-	–3.1	–3.5
HCO_3^-	–3.0	–3.4

detection limit, and *pH* range or response time. For example, the linear range (1.5×10^{-6} – 2.7×10^{-1} M), detection limit (9.0×10^{-7} M), *pH* range (2–9), conditioning time (12 h), selectivity coefficients for I^- and SCN^- (2.5×10^{-2} and 5.0×10^{-3}) of the proposed electrode is better than in a previous study [20] (8.0×10^{-6} – 1.6×10^{-1} M; 5.0×10^{-6} M; 4–9.5; 24 h; 5.0×10^{-2} ; 1.0×10^{-2} for the linear range, detection limit, *pH* range conditioning time, and selectivity coefficient for I^- and SCN^-). Moreover, it should be noted that lack of internal solution and more mechanical stability are further advantages of the proposed solid contact CGCE over usual perchlorate-selective liquid membrane electrodes reported previously [45].

Quantitative measurements of perchlorate ions in water and also urine were found to be important because of health effect of perchlorate ion in human being [46]. Thus, to assess the practical application of proposed perchlorate-selective electrodes, the PME was used in the recovery of perchlorate ions from mineral water (Damavand mineral water, marketed in Iran) and an urine sample. Different amounts of ClO_4^- ions were spiked into mineral water and also urine samples, and then the ClO_4^- contents of the samples were measured. The contents of cationic and anionic species in the mineral water (labeled

Table 4 Composition of Damavand mineral water sample

Species	Concentration / $\mu\text{g cm}^{-3}$	Species	Concentration / $\mu\text{g cm}^{-3}$
Sulfate	10.6	Potassium	0.6
Nitrate	7.5	Calcium	56.4
Fluoride	0.2	Sodium	4.6
Bicarbonate	212.0	Ammonium	0.1
Phosphate	0.1	Magnesium	15.4
Chloride	6.0		

Table 5 Determination of perchlorate ions in mineral water and human urine

Sample	Perchlorate / $\mu\text{g cm}^{-3}$		
	Added	Found	Recovery / %
Mineral water	10	9.6 ± 0.4	96.0
	100	104.1 ± 0.3	104.1
	1000	982.3 ± 0.3	98.2
Human urine	10	9.6 ± 0.7	96.0
	100	97.1 ± 0.5	97.1
	1000	978 ± 0.6	97.8

on the bottle) are given in Table 4, and the results of the analysis of the samples are given in Table 5. Obviously, the recovery is quantitative at the various perchlorate concentrations tested.

Experimental

Reagents

Reagent grade *o*-nitrophenyl octyl ether (NPOE), dioctyl sebacate (DOS), dibutyl sebacate (DBS), dimethyl sebacate (DMS), dibutyl phthalate (DBP), benzyl acetate (BA), tetrahydrofuran (THF), and high relative molecular weight PVC (all from Merck) were used as received. Sodium and potassium salt of anions (all from Merck) were of highest purity available and used without any further purification except for vacuum drying. In UV/Vis studies, sodium perchlorate was dried to ensure no water content of $NaClO_4$. Doubly distilled water was used throughout for preparing all aqueous solutions. The *pH* adjustments were made with dilute hydrochloric acid or potassium hydroxide solution as required. The platinum complexes **1–3** were synthesized according to Refs. [25, 26] and identified by means of their 1H and ^{13}C NMR.

[Pt(ρ -MeC₆H₄)₂(dppm)]: Dppm (0.42 mmol) was added to a solution of 0.4 mmol *cis*-[Pt(ρ -MeC₆H₄)₂(SMe₂)] in 20 cm³ CH₂Cl₂. The reaction mixture was stirred for 8 h at room temperature. The solvent was removed and residue was washed with acetone.

[PtMe₂(dppm)]: A freshly prepared solution of 5 cm³ dimethylmagnesium was added slowly to a stirred ice-cooled solution of [PtCl₂(dppm)] (0.54 mmol) in 20 cm³ dry ether. The reaction mixture was stirred for about 2 h and subsequently hydrolyzed with a few cm³ water. The residue was treated with *n*-hexane and the off white powder was obtained as main product.

[PtCl₂(dppm)]: [PtCl₂(SMe₂)₂] (2.5 mmol) with 2.5 mmol dppm were placed in a 50 cm³ round-bottom flask with 25 cm³ CH₂Cl₂. A white precipitate began to appear after a few seconds. The mixture was stirred at room temperature for 3 days and the white precipitate was gathered on a filter paper and washed with a few cm³ CH₂Cl₂.

Electrode preparation

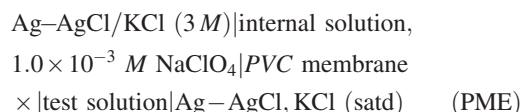
The general procedure to prepare the PVC membranes was to dissolve thoroughly 32.5 mg of powdered high molecular weight PVC, 2.6 mg of ionophore, and 64.9 mg of plasticizer in 5 cm³ THF. The resulting mixture was evaporated slowly at ambient temperature until an oily concentrated mixture was obtained. A Pyrex tube (3-mm *i.d.* on top) was dipped into the mixture for about 10 s, so that a non-transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled up from the mixture and kept at room temperature for about 6 h. The tube was then filled with an internal filling solution (1.0×10^{-3} M NaClO₄). The electrode was finally conditioned for 12 h by soaking in a 1.0×10^{-3} M NaClO₄ solution. A silver/silver chloride electrode was used as internal reference.

To prepare the coated glassy carbon electrodes (CGCE), a Metrohm glassy carbon electrode with 3 mm diameter was

used. The working surface of the electrode was polished with fine alumina slurries on a polish cloth, sonicated in distilled water, and then dried in air. The polished glassy carbon electrode was dipped into the membrane solution mentioned above, and the solvent was evaporated slowly. A thin layer of membrane was formed on the glassy carbon surface, and the electrode was allowed to stabilize under ambient conditions overnight. The electrode was finally conditioned by soaking in a $1.0 \times 10^{-3} M$ NaClO_4 solution for about 24 h. An unmodified polished glassy carbon electrode was also tested for comparative purposes, and found that it did not show any potentiometric response to perchlorate ion solutions, after the conditioning period.

Emf measurements

All *emf* measurements with the polymeric membrane electrodes (PME) and coated glassy carbon electrodes (CGCE) were carried out with the following cell assemblies:



The *emf* observations were made relative to a double-junction silver/silver chloride electrode containing a saturated solution of KCl (Metrohm) with the chamber filled with a potassium chloride solution. A silver/silver chloride electrode containing a 3 M solution of KCl was used as the internal reference electrode.

References

- Sridhar S, Collette TW, Garrison AW (1999) *Environ Sci Technol* 33:3469
- Logan BE (1998) *Biorem J* 2:69
- Greer MA, Goodman G, Pleus RC, Greer SE (2002) *Environ. Health Perspect* 110:927
- Ting D, Howd RA, Fan AM, Alexeff GV (2006) *Environ. Health Perspect* 114:881
- Baczuk RJ, Bolleter WT (1967) *Anal Chem* 39:93
- Vogel AI (1978) *Text Book of Quantitative Inorganic Analysis*, 4th edn. Longman, London, p 498
- Burns DT, Dunford MD, Sutthivaiyakit P (1997) *Anal Chim Acta* 356:141
- Weiss JA, Stanbury JB, Weiss JA, Stanbury JB (1972) *Anal Chem* 44:619
- Gallego M, Valcarcel M (1985) *Anal Chim Acta* 169:161
- Narayanan L, Buttler GW, Yu KO, Mattie DR, Fisher JW (2003) *J Chromatography B* 788:393
- Rohm TJ, Guilbault GG (1974) *Anal Chem* 46:590
- Hassan SSM, Elsaied MM (1986) *Talanta* 33:679
- Jain AK, Jahan M, Tyagi V (1987) *Analyst* 112:1355
- Coetzee CJ, Freiser H (1968) *Anal Chem* 40:2071
- Coetzee CJ, Freiser H (1969) *Anal Chem* 41:1128
- Back S (1972) *Anal Chem* 44:1696
- Fogg AG, Pathan AS, Burns DT (1974) *Analyst* 73:220
- Kataoka M, Kambara T (1976) *J Electroanal Chem* 73:279
- Sanchez-Pedreno C, Ortuno JA, Hernandez J (2000) *Anal Chim Acta* 415:159
- Shamsipur M, Soleymanpour A, Akhond M, Sharghi H, Hasaninejad AR (2003) *Sens Actuators B* 89:9
- Lizondo-Sabater J, Segui MJ, Lioris JM, Martinez-Manez R, Pardo T, Sancenon F, Soto J (2004) *Sens Actuators B* 101:20
- Zanjanchi MA, Arvand M, Akbari M, Tabatabaeian K, Zaraei G (2006) *Sens Actuators B* 113:304
- Segui MJ, Lizondo-Sabater J, Martinez-Manez R, Sancenon F, Sato J (2002) *Analyst* 127:387
- Soleymanpour A, Hamidi Asl E, Nabavizadeh SM (2007) *Sens Actuators B* 120:447
- Cooper SJ, Brown MP, Puddephatt RJ (1981) *Inorg Chem* 20:1374
- Rashidi M, Hashemi M, Khorasani-Motlagh M, Puddephatt R (2000) *J Organomet* 19:2751
- Soleymanpour A, Shamsipur M, Akhond M, Sharghi H, Nasser MA (2001) *Anal Chim Acta* 450:37
- Shamsipur M, Khayatian G, Tangestaninejad S (1999) *Electroanalysis* 11:1340
- Soleymanpour A, Hamidi E, Nasser MA (2006) *Electroanalysis* 18:1598
- Jones RO, Summerville DA, Basolo F (1979) *Chem Rev* 79:139
- Buhlmann P, Pretsch E, Bakker E (1998) *Chem Rev* 98:1593
- Malinowska E, Meyerhoff ME (1995) *Anal Chim Acta* 300:33
- Gao D, Gu J, Yu RQ, Zheng GD (1995) *Analyst* 12:499
- Malon A, Radu A, Qin W, Qin Y, Ceresa A, Maj-Zurawska M, Bakker E, Pretsch E (2003) *Anal Chem* 75:3865
- Rosatzin T, Bakker E, Simon W, Suzuki K (1993) *Anal Chim Acta* 280:197
- Bakker E, Buhlmann P, Pretsch E (1997) *Chem Rev* 97:3083
- Soleymanpour A, Shamsipur M, Akhond M, Sharghi H, Massah AR (2002) *Talanta* 58:237
- Shamsipur M, Soleymanpour A, Akhond M, Sharghi H, Hosseini Sarvari M (2004) *Electroanalysis* 17:776
- Soleymanpour A, Ahmadi Rad N, Niknam Kh (2005) *Sens Actuators B* 114:740
- Yang X, Kumar N, Chi H, Hibbert DB, Alexander PW (1997) *Electroanalysis* 9:549
- Hodinar A, Jyo A (1989) *Anal Chem* 61:1169
- Guilbault GG, Durst RA, Frant MS, Freiser H, Hansen EH, Light TS, Pungor E, Rechnitz G, Rice NM, Rhm TJ, Simon W, Thomas JDR (1976) *Pure Appl Chem* 48:127
- Umezawa Y, Umezawa K, Sato H (1995) *Pure App Chem* 67:507
- Bakker E, Pretsch E, Buhlmann P (2000) *Anal Chem* 72:1127
- Sutter J, Radu A, Peper S, Bakker E (2004) *Anal Chim Acta* 523:53
- Yu KO, Narayanan L, Mattie DR, Godfrey RJ, Todd PN, Mahle DA, Lumpkin MH (2002) *Toxicol Appl Pharmacol* 182:148