Talanta 129 (2014) 191–197

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Novel miniaturized sensors for potentiometric batch and flow-injection analysis (FIA) of perchlorate in fireworks and propellants

Saeed H.M.A. Almeer [a], Ibrahim A. Zogby [a], Saad S.M. Hassan [b,*]

[a] Central Laboratory Unit, Qatar University, P.O. Box 2713, Doha, Qatar
[b] Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt

ARTICLE INFO

Article history:
Received 3 February 2014
Received in revised form
13 May 2014
Accepted 14 May 2014
Available online 22 May 2014

Keywords:
Miniaturized planar sensors
Perchlorate
Potentiometry
Indium-porphyrin
Nitron
Methylene blue
Fireworks
Propellants
PVC membrane
Flow-injection analysis

ABSTRACT

Three planar miniaturized perchlorate membrane sensors (3×5 mm^2) are prepared using a flexible Kaptan substrate coated with nitron-perchlorate (NT-ClO_4) [sensor 1], methylene blue-perchlorate (MB-ClO_4) [sensor II] and indium-porphyrin (In-Por) [sensor III] as electroactive materials in PVC membranes plasticized with 2-NPPE. Sensors I, II and III display near-Nernstian response for 1.0×10^{-5}–1.0×10^{-2}, 3.1×10^{-5}–1.0×10^{-2} and 3.1×10^{-6}–1.0×10^{-2} mol L^{-1} ClO_4^- with lower detection limits of 6.1×10^{-6}, 6.9×10^{-6} and 1.2×10^{-6} mol L^{-1}, and anionic calibration slopes of 50.9 ± 0.4, 48.4 ± 0.4 and 57.7 ± 0.3 mV decade^{-1}, respectively. Methods for determining perchlorate using these sensors offer many attractive advantages including simplicity, flexibility, cost effectiveness, wide linear dynamic response range (0.1–1000 ppm), low detection limit ($< 1.2 \times 10^{-6}$ mol L^{-1} $\equiv$ 0.1 ppm), small sample test volume (100 μL), safety, short response time (< 20 s), long life span ($\sim$8 weeks), and extended wide working pH range (4.5–8.0). The sensors show high selectivity in the presence of some inorganic ions (e.g., PO_4^{3-}, SO_4^{2-}, $S_2O_3^{2-}$, NO_2^-, NO_3^-, N_3^-, CN^-, Cl^-, Br^-, I^-) and automation feasibility. Indium-porphyrin based membrane sensor (sensor III) is used as a detector in a wall-jet flow injection set-up to enable accurate flow injection analysis (FIA) of perchlorate in some fireworks without interferences from the associated reducing agents (sulfur and charcoal), binders (dextrin, lactose), coloring agents (calcium, strontium, copper, iron, sodium), color brighten (linseed oil) and regulators (aluminum flakes) which are commonly used in the formulations. The sensor is also used for perchlorate assessment in some propellant powders. The results fairly agree with data obtained by ion-chromatography.

1. Introduction

Perchlorates have been used as initiators, detonators, blasting agents, rocket solid propellants and military explosives. More than 40 different weapon systems or aerospace programs relied on perchlorate. Perchlorate salts were also used in fireworks, flares, automobile air bag initiator, coin-cell batteries, pyrotechnic devices, finishing leather, and electronic tubes [1]. On the other hand, perchlorate becomes a well-publicized environmental contaminant with health hazards. Perchlorate exposure can affect the function of the thyroid gland by interfering with the iodide uptake and thyroid hormone production. These health threats were the reason for setting standards by the official agencies and medical, chemical and environmental laboratories [2].

Determination of perchlorate ions has been carried out by direct or indirect methods using a variety of classical and instrumental techniques [3,4], including titrimetry [5] gravimetry [6], dye extraction spectrophotometry [7,8], atomic absorption spectrometry [9,10], ion chromatography [11,12] and electrospray ionization mass spectrometry [13]. The main drawbacks of these techniques are the low sensitivity and selectivity [5,6], the need for expensive instrumentation [11–13] and/or the extensive sample manipulation and pretreatment [7,8].

Potentiometric sensors based on the use of liquid and polymeric membranes-based ion exchangers have been utilized for perchlorate quantification. Most of these sensors incorporate electroactive perchlorate ion-association complexes with metal chelates [14–18], long chain quaternary ammonium ions [19–21] and organic dyes [22,23]. These sensors are not sensitive enough for determining low concentration levels of perchlorate in the presence of many common anions (e.g., OH^-, NO_3^-, SCN^- and I^-).

Carrier-based perchlorate selective sensors with improved selectivity and sensitivity have been advocated [24–30]. Potentiometric sensors based on the incorporation of surfactant-modified zeolite Y (SMZ) nano-clusters into poly(vinyl chloride) membranes have been also suggested for determining perchlorates [31,32].

---

* Corresponding author. Tel.: +20122216 2766; fax: +0224831836.
E-mail address: saadsmhassan@yahoo.com (S.S.M. Hassan).

http://dx.doi.org/10.1016/j.talanta.2014.05.019
0039-9140/

However, the development of miniaturized perchlorate sensors with enhanced sensitivity and improved selectivity is still an urgent demand to deal with small sample sizes and to avoid the hazardous effect of these substances.

The present study describes the preparation, characterization of simple miniaturized planar, sensitive and cost effective potentiometric poly (vinyl chloride) matrix membrane sensors for fast determination of perchlorates. The sensing membranes incorporate [(nitron$^+$) (ClO_4^-)] and [(methylene blue$^+$) (ClO_4^-)] ion-pair complexes and [indium-porphyrin] charged carrier complex. Miniaturized chip based on the use of [indium-porphyrin] (In-Por) membrane is used for batch determination of perchlorates in fireworks and propellant samples and in a flow-injection manifold for continuous perchlorate assay.

2. Experimental

2.1. Equipment

Planar miniaturized ClO_4^- ion-PVC membrane sensors in conjunction with an Orion Ag/AgCl double junction reference electrode (model 90-02) filled with 10% (w/v) K_2SO_4 in the outer compartment were used for the potentiometric measurements. An Orion pH/meter (model SA 720) and a combination Ross glass pH electrode (Orion 81-02) were used. The cell used for EMF measurements at 25 ± 1 °C was of the type: Ag/AgCl/KCl (10^{-2} mol L^{-1})/sample test solution/sensor membrane/internal filling solution/AgCl/Ag.

Continuous ClO_4^- assay was performed using a flow-injection analysis (FIA) manifold consisting of a two-channel Ismatech peristaltic pump (MS-REGLO model). Polyethylene tubing (0.7 mm i.d.), an Omnifit injection valve (Omnifit, Cambridge, UK) with a sample loop of 100 μL volume and a home-made high-impedance data acquisition 8-channel box connected to a PC through the interface ADC 16 (Pico Tech., UK) and PicoLog for windows (version 5.07) software were used for recording the potential signals.

Ion chromatography measurements of perchlorate samples were conducted for comparison using a Dionex DX-500 system equipped with GP50 gradient pump and ED40 electrochemical conductivity cell detector. A Dionex IonPac AS-16 separation column (2×250 mm^2), AS16 guard column (2×50 mm^2), 5×10^{-2} mol L^{-1} NaOH eluent, 0.5 mL flow rate and 500 μL perchlorate injection volume were used.

2.2. Reagents

Unless otherwise specified, all chemicals used were of the highest purity and deionized bi-distilled water was used for the preparation of the reagents and test solutions. High molecular weight poly (vinyl chloride) (PVC), *o*-nitrophenylphenyl ether (2-NPPE), tetrahydrofuran (THF), sodium perchlorate, nitron and methylene blue were purchased from Sigma-Aldrich Inc. (St. Louis, MO, USA). Selectivity coefficient measurements of the interfering ions were conducted with sodium and potassium salts of all the tested anions. Indium (III)-5,10,15,20-tetraphenylporphyrinato was synthesized and purified according to the previously described method [33].

2.3. Planar miniaturized perchlorate sensor

A flexible (13.5×3.5 mm^2) polyimide (Kaptan, ®DuPont) substrate (125 μm thick) was sputtered with gold to give 3×5 mm^2 gold base electrode. The electrode was covered with silver metal as described previously [34]. An electrical wire was connected to the electrode by means of Ag-epoxy (Epoxy Technology). The electrical contact was insulated using silicone rubber coating seal (Dow Corning 3140TV). The electrode was coated with the sensing membranes. A poly(vinyl chloride) membrane cocktail was prepared as previously described [35,36] with the composition: 2.9 mg of the ionophore, 66.5 mg PVC, and 127 mg of *o*-nitophenylphenyl ether (2-NPPE) solvent mediator. The membrane ingredients were thoroughly mixed in a Petri dish (3 cm diameter) and dissolved in 3 mL of dry freshly distilled THF. The homogeneous solution obtained was used for coating the electrode using a microsyringe for successive application of few micro-liters of the sensing solution. The electrode was left to dry in the air for one minute before repeating further addition (~5 times) of the sensing solution. The coated end of the sensor was protected from damage by insertion in 1 mL blue tip micropipette cut at its end to allow solutions contact.

A single channel wall-jet flow-injection system incorporating the prepared sensor was used for continuous measurements. A peristaltic pump was used to propel the carrier solution (1.0×10^{-1} mol L^{-1} phosphate buffer of pH 5.5) through PTEE tubing (1.1 mm i.d.) at a flow rate of 1.7 mL min^{-1}. The tubing was ended with a horizontally mounted 8 cm long glass capillary tube (2.6 mm o.d, 1.0 mm i.d). The length of the tubing from the injection valve to the capillary tube was 25 cm. The free end of the capillary tube was cut at 90°. This end of tube was brought into contact with the sensing part of the sensor. The miniature sensor was mounted in a vertical position with a connection wire directed upward, placed in conjunction with a double junction Ag/AgCl reference electrode in a Petridish where the level of solution was kept above the sensor surface (Fig. 1). The distance between the end of the capillary tube and the sensing surface of the sensor was

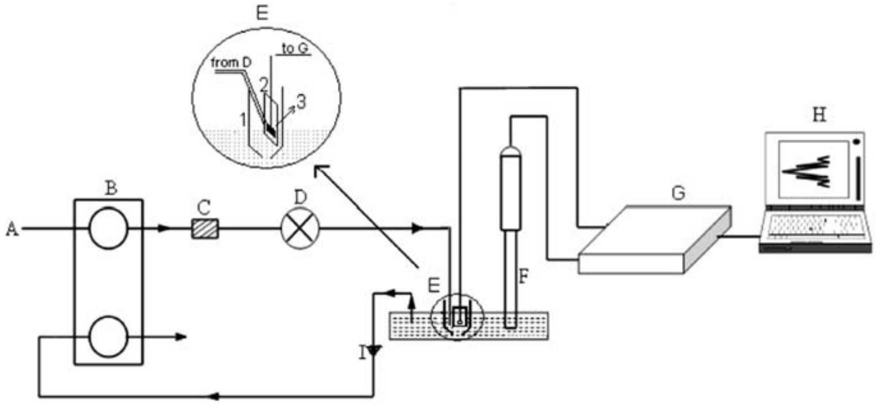


Fig. 1. Schematic diagram of the two channel flow injection manifold used for perchlorate measurements: (A) 1.0×10^{-1} mol L^{-1} phosphate buffer (pH 5.5) carrier; (B) peristaltic pump; (C) pulse damper; (D) sample injection valve; (E) flow injection detector; [(1) micropipette tip, (2) polyimide microchip; (3) PVC sensing membrane]; (F) reference electrode; (G) data acquisition system; and (H) laptop computer.

5 mm. The detector was conditioned by soaking in 1.0×10^{-2} mol L^{-1} solution of $NaClO_4$ for 1–2 h before use and stored dry in air when not in use.

2.4. Sensor calibration

Aliquots (1.0 mL) of 1.0×10^{-1}–1.0×10^{-6} mol L^{-1} aqueous solutions of ClO_4^- were transferred to 50 mL beakers containing 9.0 mL de-ionized double distilled water or 1.0×10^{-1} mol L^{-1} phosphate buffer solution of pH 5.5. The sensor in conjunction with a double junction Ag/AgCl reference electrode was inserted into the solutions. The potential readings of the stirred solution were recorded after stabilization to ±0.5 mV. The emf readings were plotted as a function of logarithm ClO_4^- concentrations. The calibration graph was used for subsequent determination of unknown perchlorate concentrations.

2.5. Effect of pH and response time

Variation of the potential response of the sensor as a function of pH change was tested by measuring the potentials of 1.0×10^{-3} and 1.0×10^{-4} mol L^{-1} perchlorate solutions of various pH values. The pH of the solutions was changed by adding small aliquots of concentrated NaOH and/or HCl solutions. The corresponding mV readings were recorded after each addition and plotted against the corresponding pH. The response time of the sensors was measured in constantly stirred 1.0×10^{-2}–1.0×10^{-6} mol L^{-1} perchlorate solutions. The stability of the potential was measured for different concentrations of perchlorate during a 5 min period for each concentration. The relation between mV readings and time was plotted.

2.6. Effect of interfering ions

The standard separate solutions method [37] was applied for measuring the potentiometric selectivity coefficients ($K^{Pot}_{ClO_4,B}$) of the sensor using 1.0×10^{-3} mol L^{-1} solutions. Eq. (1) was used for calculation.

$$K^{Pot}_{ClO_4,B} = a_{ClO_4}/(a_B)^{Z_{ClO4}/Z_B} \tag{1}$$

where, a_{ClO4} is the activity of perchlorate ion, a_B is the activity of the interfering ion, and Z_{ClO4} and Z_B are the charges of the perchlorate and interfering ions, respectively.

2.7. Direct potentiometric determination of perchlorate ions

Perchlorate miniaturized membrane sensors based on $[(NT^+)(ClO_4^-)]$, $[(MB^+)(ClO_4^-)]$ or [In-Por] and Ag/AgCl double junction reference electrode were immersed into a 25 mL beaker containing 10 mL aliquot of 1.0×10^{-1} mol L^{-1} phosphate buffer of pH 5.5. The solution was stirred till a stable potential response within ±0.2 mV was obtained, followed by addition of 0.10–1.00 mL portions of the unknown perchlorate test solutions. The potential response of the sensor was measured after stabilization and compared with the calibration curve.

2.8. Flow-injection analysis (FIA) of perchlorate

Using an Omnifit injection valve (Rheodyne, Model 7125), successive portions (100 μL) of the unknown perchlorate solutions were injected in a carrier solution consisting of 1.0×10^{-1} mol L^{-1} phosphate buffer of pH 5.5 and propelled at a flow rate of 1.7 mL min^{-1} by means of the peristaltic pump. All connections were made using Tygon tubing (1.1 mm i.d.). The planar sensor in conjunction with a Ag/AgCl double junction reference electrode was used as a detector. Data recording and manipulation of the output signals were made with PC based ADC-16 high resolution data logger (Pico Technology, UK). Repeated injection and recording of the signals for each sample were carried out and the average potential value at the maximum signal height for each run was recorded. The potentials were compared with a calibration graph (signal potential vs log $[ClO_4^-]$) similarly obtained under identical conditions using 1.0×10^{-5}–1.0×10^{-1} mol L^{-1} of standard perchlorate solutions.

2.9. Determination of perchlorate in fireworks

The contents of two firework shells were transferred to an agate mortar and thoroughly homogenized and dried at room temperature under vacuum for one hour. Approximately 0.5–1.0 g of the powder was accurately weighed and transferred to a 100 mL beaker. The solid sample was dissolved in ~50 mL of deionized bi-distilled water and the mixture was carefully heated at 60 °C on a water-bath for 5 min to extract the perchlorates. The solution was cooled down to ambient temperature, filtered, and completed to 100 mL with deionized bi-distilled water.

The perchlorate content in the test solution was potentiometrically measured as described above. For ion chromatography (IC) measurements of perchlorate, typically 15 mL of the above final test solution was further diluted to 100 mL. Prior to analysis, approximately 5 mL of the solution was filtered using 40 μm filter disk and 100 μL aliquots were injected into the chromatographic column.

3. Results and discussion

3.1. Characteristics of the sensors

Reagents known to precipitate perchlorate ion (acyclic and cyclic quaternary amines) such as methylene blue and nitron and perchlorate coordinating metalloporphyrin (e.g., indium(III)-porphyrin) were selected and tested as ionophores in PVC membrane sensors responsive for perchlorate ion.

Planar miniaturized polymeric membrane sensors based on nitron perchlorate ($NT\text{-}ClO_4$), methylene blue-perchlorate ($MB\text{-}ClO_4$) and indium porphyrin (In-Por) (Fig. 2) with *o*-nitrophenylphenyl ether (2-NPPE) as a plasticizer were prepared. The sensors were evaluated under batch and continuous mode of operations. Sensors based on ($NT\text{-}ClO_4$), ($MB\text{-}ClO_4$) and (In-Por) membranes with the composition: 1.8 wt% ionophore, 33.6 wt% PVC and 64.6 wt% 2-NPPE plasticizer exhibited linear responses to ClO_4^- ions within the concentration ranges 1.0×10^{-5}–1.0×10^{-2}, 3.1×10^{-5}–1.0×10^{-2} and 3.1×10^{-6}–1.0×10^{-2} mol L^{-1} with lower detection limits of 6.1×10^{-6}, 6.9×10^{-6} and 1.2×10^{-6} mol L^{-1} respectively. Membranes plasticized with other solvent mediators (e.g., dioctylphthalate and dibutylsebacate) showed poor response for ClO_4^- ions, probably because of the increased polarity, viscosity and density of 2-NPPE and its high dissolving power of the tested ionophores over the other solvent mediators.

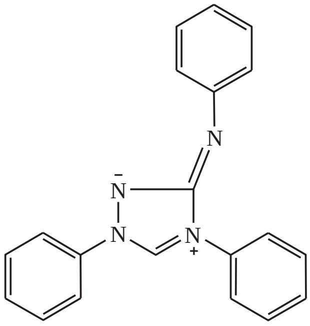
An electrochemical evaluation of the sensors according to the IUPAC recommendations [37] and a validation of the perchlorate assay method were made. The performance characteristics of the proposed sensors under batch conditions, based on data collected over a period of 3 months with 3 different assemblies for each sensor, are given in Table 1. The dynamic response times of the three sensors to reach ~95% of equilibrium response, were 15–20 s.

Fig. 3 presents the calibration plots of these sensors. Calibration slopes of 50.9 ± 0.4, 48.4 ± 0.4 and 57.7 ± 0.3 mV $decade^{-1}$ were obtained with sensors I, II and III, respectively. Least square analysis of the data for the sensors I (NT-ClO_4), II (MB-ClO_4) and III (In-Por) gave the following relations, respectively:

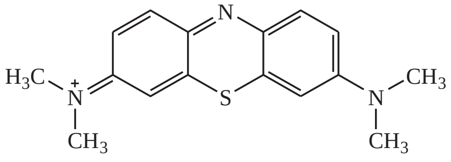
$$E\,(\mathrm{mV}) = (-50.9 \pm 0.4)\log\,[\mathrm{ClO_4}^-] + (389.8 \pm 0.3) \quad (2)$$

$$E\,(\mathrm{mV}) = (-48.4 \pm 0.4)\log\,[\mathrm{ClO_4}^-] + (279.7 \pm 0.3) \quad (3)$$

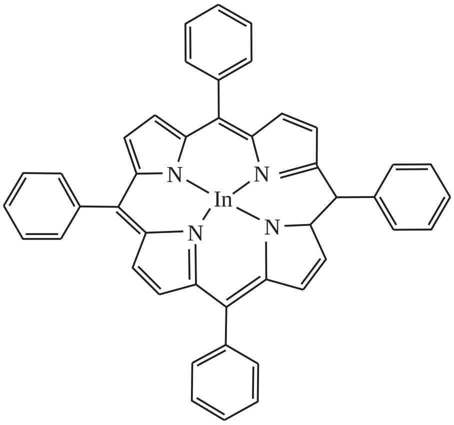
$$E\,(\mathrm{mV}) = (-57.7 \pm 0.3)\log\,[\mathrm{ClO_4}^-] + (392.8 \pm 0.3) \quad (4)$$



Nitron



Methylene blue



Indium (III)-porphyrin

Fig. 2. Chemical structures of perchlorate electroactive materials used for perchlorate membrane sensors.

Student's (t) value was calculated from data obtained using Eq. (5) for repeated measurements (n=6) of 10 μg mL^{-1} internal quality control perchlorate sample under batch mode of operation. At 95% confidence level, the t_{exp} was 0.898 compared with the theoretical tabulated value (t=2.015) indicating that the null hypothesis was retained.

$$t_{exp} = [(\mu - x)\sqrt{n}]/s \quad (5)$$

where μ is the concentration of the internal quality control sample used in the test (i.e., 10 μg mL^{-1}), x is the average concentration found, n is the number of analyte replicates (i.e., 6) and s is the standard deviation of measurements.

3.2. Method accuracy and precision

The accuracy, precision, within-day repeatability, between-days reproducibility and relative standard deviation for all measurements were calculated [38,39] and the results are listed in Table 1.

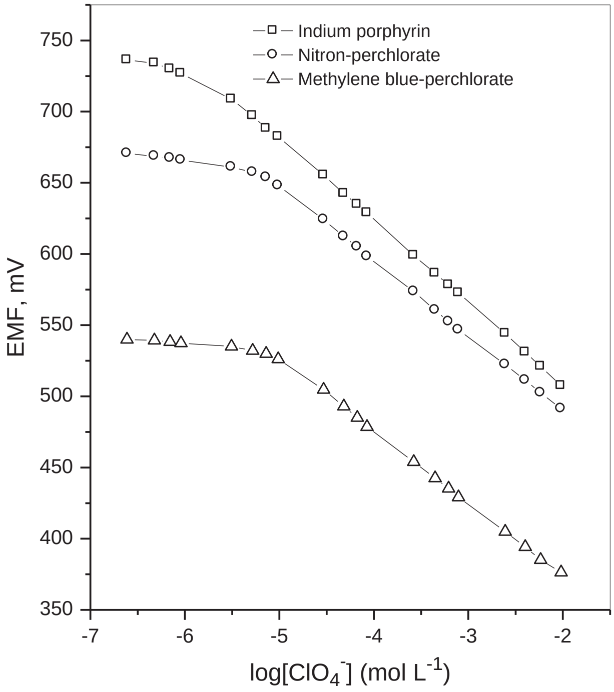


Fig. 3. Potentiometric calibration plot of perchlorate ions using miniaturized PVC based membrane sensors in 1.0 × 10^{-1} mol L^{-1} phosphate buffer of pH 5.5 as a background solution.

Table 1
Potentiometric response characteristics of miniaturized perchlorate PVC membrane sensors under batch mode of operation.

Parameter[a]	Sensor-I (NT-ClO_4)	Sensor-II (MB-ClO_4)	Sensor-III (In-Por)
Slope (mV decade^{-1})	50.9 ± 0.4	48.4 ± 0.4	57.7 ± 0.3
Lower detection limit (mol L^{-1})	6.1 × 10^{-6}	6.9 × 10^{-6}	1.2 × 10^{-6}
Linear range (mol L^{-1})	1.0 × 10^{-5}–1.0 × 10^{-2}	3.1 × 10^{-5}–1.0 × 10^{-2}	3.1 × 10^{-6}–1.0 × 10^{-2}
Working acidity range (pH)	3.0–9.5	2.5 – 8.0	4.5–8.5
Response time (s)	< 20	< 20	20 <
Correlation coefficient (r^2)	0.999	0.999	0.999
Standard deviation (mV)	0.57	0.96	1.01
Life span (week)	8	8	8
Precision (%)	2.1	2.3	1.9
Accuracy (%)	98.8	98.9	99.7
Within-day-reproducibility (%)	1.2	1.2	1.3
Between-day-reproducibility (%)	2.2	2.4	2.2

[a] Mean of 6 measurements.

3.3. Effects of pH

Potential-pH relations of ClO_4^- membrane sensors based on ($NT\text{-}ClO_4$), ($MB\text{-}ClO_4$) and (In-Por) revealed that within the pH range of 4.5–8, the potentials did not vary by more than ±1 mV. At lower pH range ($pH < 3$) and higher pH range ($pH > 8$), the potential readings sharply decreased probably due to the interferences of H^+ and OH^- ions, respectively. At low pH values, H_3O^+ along with the formation of $H_2ClO_4^+$ species were probably extracted in the membrane phase and compete with ClO_4^- ion for the cationic site in the membrane. At high pH values, the ionophore at the membrane surface was probably dissociated or decomposed. Hydroxide ions may also compete with ClO_4^- for metal porphyrin chelation. This is in a good agreement with the findings of other workers that the response of some metalloporphyrin potentiometric anion sensors is hardly affected by pH changes in the range of 3–8 [40,41]. All subsequent potentiometric measurements of ClO_4^- ions were made in 1.0×10^{-1} mol L^{-1} phosphate buffer background of pH 5.5.

3.4. Sensor selectivity

The interfering effect of some different anion species was potentiometrically evaluated by measuring the selectivity coefficients of the sensors for these ions using the standard separate solutions method (SSM) [37]. The mixed solutions method was not used to avoid partial oxidation of most interfering anions (SCN^-, I^-, N_3^-, Br^-, NO_2^-, CN^-, $S_2O_3^{2-}$). The results revealed that with the exception of SCN^- and I^- ions, high concentrations of most common anions, did not affect the selectivity of the sensors. Nitron-ClO_4 based membrane sensor exhibited a selectivity order: $ClO_4^- > SCN^- > I^- > NO_3^- > N_3^- = Br^- > NO_2^- > CN^- > Cl^- = S_2O_3^{2-} > SO_4^{2-} = PO_4^{3-}$. For methylene blue-$ClO_4$ based membrane sensor, the order of selectivity was: $ClO_4^- > SCN^- > I^- > NO_3^- > Br^- = N_3^- > NO_2^- = CN^- > Cl^- > S_2O_3^{2-} > SO_4^{2-} = PO_4^{3-}$ ions. The order of selectivity for indium-porphyrin based membrane sensor was: $SCN^- > ClO_4^- > I^- > NO_2^- > Br^- = N_3^- > Cl^- > NO_3^- > CN^- > S_2O_3^{2-} > SO_4^{2-} = PO_4^{3-}$ (Table 2).

It can be seen that membrane containing quaternary amine ion exchangers (nitron and methylene blue) typically behave according to Hofmeister order of decreasing anion hydrophobicity. Membrane containing indium-porphyrin ionophore showed selectivity sequence similar to that reported with some metalloporphyrin ionophores [42,43].

It is well established that the selectivity pattern of potentiometric membrane sensors is mainly influenced by: (i) the presence of lipophilic ionic additives (nature and concentration) in the membrane composition, (ii) purity of membrane polymer and plasticizer (the presence of ionic impurities), (iii) type of binding mechanism of the electroactive ionophore (neutral carrier, charged carrier, ion exchanger), and (iv) pH of the test solutions.

Table 2
Potentiometric selectivity coefficients ($K^{Pot}_{ClO_4,B}$) of some common anion species using miniaturized perchlorate sensors.

Interferent, B	Sensor-I ($NT\text{-}ClO_4$)	Sensor-II ($MB\text{-}ClO_4$)	Sensor-III (In-Por)
SCN^-	−0.1	−0.1	0.2+
I^-	−2.4	−2.8	−2.1
NO_3^-	−2.8	−3.0	−3.9
N_3-	−3.2	−3.1	−3.7
NO_2^-	−3.4	−3.3	−2.7
CN^-	−3.5	−3.4	−4.1
Br^-	−3.2	−3.1	−3.7
Cl^-	−3.7	−3.6	−3.9
$S_2O_3^{2-}$	−3.7	−3.6	−4.4
SO_4^{2-}	−3.8	−3.8	−4.7
PO_4^{3-}	−3.8	−3.8	−4.7

A further study was made by incorporating ionic additives in the sensor membranes. Membrane composition containing anionic and cationic additives such as tetrakis (*p*-chlorophenyl) borate (KT*p*ClPB) and tridodecylmethyl-ammonium chloride (TDMAC), respectively, in separate experiments were tested in the level of 50 mol% relative to indium porphyrin ionophore in the sensor membrane. The results with DMAC, revealed that a typical Hofmeister anion selectivity pattern was obtained with slight effect on the order and magnitude of the selectivity coefficient values, sensitivity and lower detection limit. On the other hand, incorporation of KT*p*ClPB showed anti Hofmeister trend with enhanced response for chloride and nitrite ions. This confirmed the proposed charged carrier mechanism and in a good agreement with some previous reports [44,45]. Since chloride ion is the main decomposition product and associated impurity with perchlorate, anionic additives was avoided to circumvent possible interference of the chloride ion.

3.5. Response mechanism

Indium (III)-porphyrin ionophore interacts with perchlorate and other complexing anions with subsequent increasing of the coordination number of indium from 3 to 5 or 6. In addition, the electron density on the central indium metal of porphyrin complex varies by the extent of electron donation from the donor atoms of the equatorial ligands. Consequently, different binding affinities of indium porphyrin with perchlorate and other anions are expected.

Indium-porphyrin based membrane sensor displayed the highest selectivity towards perchlorate in the presence of many of the tested interfering ions compared with the other two examined sensors. It has been reported that indium-porphyrin reacts with perchlorate to form mono- and di-perchlorate species at the axial position without further complexation with other anions [41]. It seems that at the membrane/sample interface, perchlorate ion selectively coordinates with the central In (III).

Fig. 4 illustrates the possible two mechanisms responsible for the anion response of In (III)-porphyrin based membrane sensor. In the neutral carrier mechanism (Fig. 4A), perchlorate anion in the aqueous sample solution can be extracted into the membrane phase as a sixth ligand of the neutral indium mono-perchlorate yielding a negatively charged indium di-perchlorate complex. In the charged carrier mechanism (Fig. 4B), the phase boundary potentials generated due to the interaction of indium-porphyrin charged molecule and the perchlorate anion lead to the formation of indium mono-perchlorate neutral molecule. Since the latter mechanism did not involve formation of strong σ-bonded In (III)-porphyrin, it is possible to suggest that the charged carrier

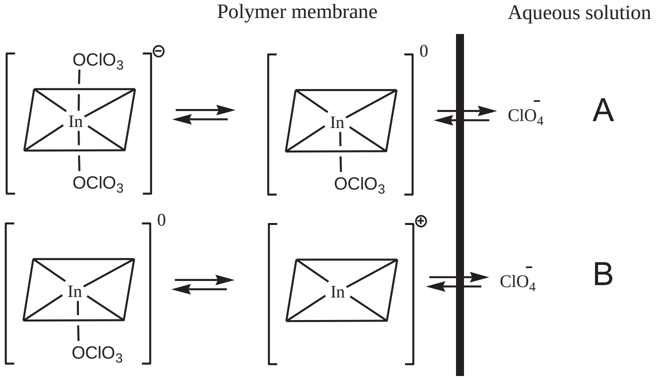


Fig. 4. Response mechanism of miniaturized perchlorate PVC membrane sensors; (A) neutral carrier mechanism, and (B) charged carrier mechanism.

concept may be the predominant mechanism. It is worth mentioning that some metal porphyrins can change the mechanism of response from charged carrier to neutral carrier by changing the pH of the test sample [42].

3.6. Optimization of the FIA method

Flow-injection analysis of perchlorate was examined using the developed planar miniaturized membrane sensor incorporating indium-porphyrin ionophore in conjunction with a wall-jet cell. A phosphate buffer solution of pH 5.5 (1.0×10^{-1} mol L^{-1}) was utilized as a carrier and various sample volumes (5–600 μL), rate of carrier flow (0.2–3.5 mL min^{-1}) and tubing size (0.5–1.8 mm) were tested. As the sample volume increased, the peak heights and residence time increased with a decrease of sample throughput. The optimum conditions were, sample volume: 100 μL, flow rate: 1.5 mL min^{-1} and tubing size: 1.1 mm i.d. Under these conditions, the linear operational range led to an analysis output of ~60 samples per hour. Typical response signals were obtained and shown in Fig. 5. An evaluation of the performance characteristics of indium-porphyrin miniaturized membrane sensor under optimal flow injection mode of operations revealed fast response, high sensitivity, good stability, and reasonable selectivity (Table 3).

Standard solutions containing 1.0×10^{-1}–1.0×10^{-5} mol L^{-1} ClO_4^- were determined ($n=3$) using the described FIA setup and the optimized experimental conditions. The method detection limit (MDL) calculated by the equation: MDL=αs, (where $\alpha=3.14$ and s is the standard deviation) was 8.5×10^{-6} mol L^{-1} ClO_4^- and the average signal-to-noise ratio (S/N) was 56/1.

An internal QC certified perchlorate sample (10 μg mL^{-1}) was spiked into different test samples and the recovery was calculated using Eq. (6).

$$\text{Recovery\%} = [(x_s - x)/x_{add}]100 \tag{6}$$

where x_s and x are the difference between the mean concentration of the spiked and un-spiked samples and x_{add} is the spiked concentration of the reference sample. An average recovery of 98.7% and a mean precision of 2.3% ($n=6$) were obtained. Student's t-value at 95% confidence level was calculated using a certified reference perchlorate sample (10.0 μg mL^{-1}) under FIA mode of operation ($n=6$). The calculated experimental value ($t_{exp}=0.625$) was much less than the tabulated critical value ($t=2.015$).

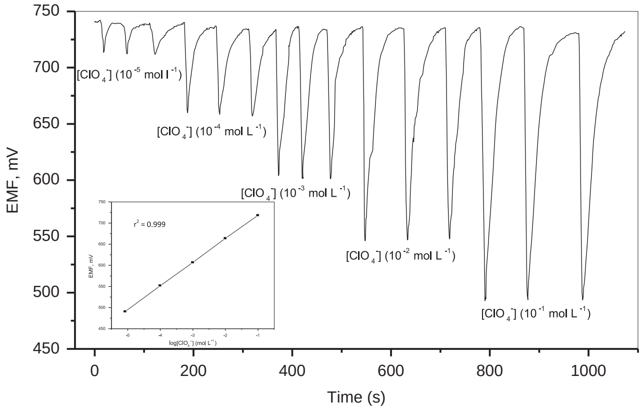


Fig. 5. FIA potential/time trace of 1.0×10^{-1}–1.0×10^{-5} mol L^{-1} perchlorate and the calibration plot using indium-porphyrin PVC membrane miniaturized sensor.

Table 3
Potentiometric response characteristics of miniaturized perchlorate based PVC membrane sensors under hydrodynamic (FIA) mode of operations.

Characteristics	Value[a]
Calibration slope (mV decade^{-1})	55 ± 0.6
Correlation coefficient (r^2)	0.999
Linear response range (mol L^{-1})	5.0×10^{-5}–1.0×10^{-2}
Lower detection limit (mol L^{-1})	8.5×10^{-6}
Acidity working range (pH)	4.5–8.5
Operational life time (week)	8
Residential time, T (s)	10–20
Travel time, t_a (s)	10–11
Return time, T' (s)	30–90
Base to baseline time, ΔT (s)	50–98

[a] Mean of 6 measurements.

3.7. Determination of perchlorate in hazardous materials

Perchlorate ions in some commercial fireworks were determined under static and hydrodynamic (FIA) modes of operations using the miniaturized indium (III)-porphyrin PVC based membrane sensor and 1.0×10^{-1} mol L^{-1} phosphate buffer of pH 5.5 as a background or carrier solution. Since most of the commercial fireworks formulations consist of > 50% additives, the response of the perchlorate sensor for some of these constituents was tested.

No interferences were caused by 100-fold excess of some reducing agents (sulfur and charcoal), binders (dextrin, lactose), coloring agents (calcium, strontium, copper, iron, sodium), color brighten (linseed oil) and regulators (aluminum flakes). Table 4 presents the results obtained for determination of perchlorate content of some commercial fireworks using the proposed potentiometric technique and the standard ion chromatography for comparison. An F-test showed no significant difference at 95% confidence level between means and variances of the potential of set of results. The calculated F-value ($n=6$) was in the range of

Table 4
Potentioetric determination of perchlorate in some fireworks using miniaturized indium (III)-porphyrin based PVC membrane sensor under batch and FIA mode of operations.

Fireworks	[ClO_4^-] (%)[a]			F-test[b]	
	Potentiometry		Chromatography	Batch	FIA
	Batch	FIA			
Sample I	33.1 ± 2.6	32.7 ± 2.2	31.9 ± 1.9	1.873	1.341
Sample II	37.8 ± 2.1	37.2 ± 2.7	36.7 ± 2.4	1.306	1.266
Sample III	43.1 ± 2.7	42.9 ± 2.9	41.9 ± 2.4	1.266	1.460

[a] Average of 6 measurements.
[b] Critical tabulated F-value ($n=6$) at 95% confidence interval=5.05.

Table 5
Direct potentiometric determination of perchlorate in some propellants using miniaturized indium (III)-porphyrin based PVC membrane perchlorate sensor under batch and FIA mode of operations.

Compound	[ClO_4] (%)			RSD (%)		Test[b]	
	Calculated	Found[a]		Batch	FIA	Batch	FIA
		Batch	FIA				
Guanidine perchlorate	62.4	61.8	62.1	±3.2	±2.7	0.406	0.245
Urea perchlorate	62.0	60.9	61.6	±2.2	±2.9	1.158	0.355
Hydrazine perchlorate	75.1	74.4	74.6	±2.7	±3.2	0.608	0.337
Ethylenediamine perchlorate	62.0	61.1	60.4	±2.4	±2.8	0.888	1.426
Ethylamine perchlorate	68.4	67.8	67.8	±3.1	±3.0	0.482	0.498
Ammonium perchlorate	84.7	83.9	83.9	±2.1	±2.3	0.945	0.788

[a] Average of 6 measurements.
[b] Critical tabulated t-value ($n=6$) at 95% confidence interval=2.015.

$F=1.3$–1.9 (batch) and 1.3–1.5 (FIA) compared with the critical tabulated value ($F=5.05$).

Perchlorate ions were also determined in some pure propellant powders of purity $>99\%$ under batch and FIA mode of operations. The differences between the calculated and found values did not exceed ~3.2% indicating close agreement and good reliability of the proposed sensor. Data obtained by the batch and FIA methods showed no statistical difference between the theoretical Student's test ($t=2.015$) and the calculated values for batch ($t_{exp}=0.406-1.126$) and FIA ($t_{exp}=0.245-1.426$). The results are shown in Table 5.

3.8. Advantages and comparison with other methods

Many of the previously suggested methods for perchlorate measurements suffer from some limitations such as the poor sensitivity and selectivity [5,6], the limited range of measurement, the need for expensive instrumentation [11–13] and/or the time consuming for sample manipulation and pretreatment [7,8]. The present sensor covers a wide concentration range, displays low detection limit [14,17,29], requires no prior sample pretreatment step and exhibits high selectivity [28–30]. In addition, inherent advantages offered by the present technique are the use of small sample volume (100 μL), to avoid any hazardous effect and to ensure safety, automation feasibility, high analytical throughput (~60 sample h^{-1}), good response stability ($< \pm 1$ mV), high precision ($\pm 0.7\%$), low cost, reasonable selectivity in the presence of many interfering ions, applicability for turbid and colored solutions over a wide range of perchlorate concentrations (1.0×10^{-2}–1.0×10^{-6} mol L^{-1}) with a detection limit of 2.0×10^{-6} mol L^{-1} ($\equiv 0.1$ ppm) at pH 5.5.

4. Conclusions

A novel miniaturized sensor (3×5 mm^2) consisting of indium-porphyrin as electroactive material in plasticized PVC membranes was prepared, characterized under static (batch) and hydrodynamic (FIA) mode of operations. The sensor was used for perchlorate assay in some fireworks and propellant powders. The assay methods were validated and the results were compared with data obtained by ion chromatography. The linear response range, detection limit, life span, potential stability, response time, accuracy and selectivity of the proposed sensor are better than many of those previously suggested sensors. The sensor was used for automated measurement of perchlorate ions in microliter quantities of some real hazardous samples.

References

[1] P.G. Thorne, Field Screening Method for Perchlorate in Water and Soil, US Army Corps of Engineers, NTIS, Springfield, Virginia, 2004.
[2] E.T. Urbansky, ESPR—Environ. Sci. Pollut. Res. Int. 9 (2002) 187–192.
[3] V.V. Goncharuk, O.V. Zui, N.F. Kushchevskaya, J. Water Chem. Technol. 31 (2009) 186–194.
[4] E.T. Urbansky, Crit. Rev. Anal. Chem. 30 (2000) 311–343.
[5] R.J. Baczuk, W.T. Bolleter, Anal. Chem. 39 (1967) 93–95.
[6] A.I. Vogel, Text Book of Quantitative Inorganic Analysis, 4th ed., Longman, London (1978) 498.
[7] J.A. Weiss, J.B. Stanbury, Anal. Chem. 44 (1972) 619–620.
[8] D.T. Burns, N. Chimpalee, M. Harrott, Anal. Chim. Acta 217 (1989) 177–181.
[9] M. Gallego, M. Valcarcel, Anal. Chim. Acta 169 (1985) 161–169.
[10] S. Chattaraj, K. De, A.K. Das, Mikrochim. Acta 106 (1992) 183–190.
[11] L. Narayanan, G.W. Buttler, K.O. Yu, D.R. Mattie, J.W. Fisher, J. Chromatogr. B 788 (2003) 393–399.
[12] J.D. Lamb, D. Simpson, B.D. Jensen, J.S. Gardner, Q.P. Peterson, J. Chromatogr. A 1118 (2006) 100–105.
[13] E.T. Urbansky, M.L. Magnuson, D. Freeman, C. Jelks, J. Anal. At. Spectrom. 14 (1999) 1861–1866.
[14] N. Ishibashi, H. Kohara, Anal. Lett. 4 (1971) 785–792.
[15] T.J. Rohm, G.G. Guilbault, Anal. Chem. 46 (1974) 590–592.
[16] A.C. Wilson, K.H. Pool, Talanta 23 (1976) 387–388.
[17] S.S.M. Hassan, M.M. Elsaied, Talanta 33 (1986) 679–684.
[18] K. Jain, M. Jahan, V. Tyagi, Anal. Chim. Acta 231 (1990) 69–75.
[19] C.J. Coetzee, H. Freiser, Anal. Chem. 41 (1969) 1128–1130.
[20] S. Back, Anal. Chem. 44 (1972) 1696–1698.
[21] A.G. Fogg, A.S. Pathan, D.T. Burns, Anal. Chim. Acta 73 (1974) 220–223.
[22] M. Kataoka, T. Kambara, J. Electroanal. Chem. 73 (1976) 279–284.
[23] C. Sanchez-Pedreno, J.A. Ortuno, J. Hernandez, Anal. Chim. Acta 415 (2000) 159–164.
[24] F. Gholamian, M.A. Sheikh-Mohseni, M. Salavati-Niasari, Mat. Sci. Eng. (C) 31 (2011) 1688–1691.
[25] B. Rezaei, S. Meghdadi, S. Bagherpour, J. Hazard. Mater. 161 (2009) 641–648.
[26] M.J. Segui, J. Lizondo-Sabater, R. Martinez-Manez, F. Sancenon, J. Soto, E. Garcia-Breijo, l. Gil, Sensors 6 (2006) 480–491.
[27] M.R. Ganjali, M. Yousefi, T. Poursaberi, L. Naji, M. Salavati-Niasari, M. Shamsipur, Electroanalysis 15 (2003) 1476–1480.
[28] M. Shamsipur, A. Soleymanpour, M. Akhond, H. Sharghi, A.R. Hasaninejad, Sens. Actuators B 89 (2003) 9–14.
[29] J. Lizondo-Sabater, M.J. Segui, J.M. Lioris, R. Martinez-Manez, T. Pardo, F. Sancenon, J. Soto, Sens. Actuators B 101 (2004) 20–27.
[30] M.A. Zanjanchi, M. Arvand, M. Akbari, K. Tabatabaeian, G. Zaraei, Sens. Actuators B 113 (2006) 304–309.
[31] A. Nezamzadeh-Ejhieh, A. Badri, J. Electroanal. Chem. 660 (2011) 71–79.
[32] A. Nezamzadeh-Ejhieh, A. Badri, Anal. Bioanal. Electrochem. 3 (2011) 565–586.
[33] A.D. Alder, F.R. Longo, F. Kampas, J. Kim, Inorg. Nucl. Chem. 32 (1970) 2443–2445.
[34] S.A. Marzouk, V.V. Cosofret, R.P. Buck, H. Yang, W.E. Cascio, S.S.M. Hassan, Talanta 44 (1997) 1527–1541.
[35] S.S.M. Hassan, E.M. Elnemma, A.H.M. Kamel, Talanta 66 (2005) 1034–1041.
[36] S.S.M. Hassan, N.M.H. Rizk, Analyst 122 (1997) 815–819.
[37] Y. Umezawa, P. Buhlmann, K. Umezawa, K. Tohda, S. Amemiya, Pure Appl. Chem. 72 (2000) 1851–2082.
[38] J.K. Taylor, Quality Assurance of Chemical Measurements, CRC Press, Florida, 1987.
[39] J.R. Taylor, An Introduction to Error Analysis: The Study of Uncertainties in Physical Measurements, University Science Books, USA, 1999.
[40] M. Shamsipur, M. Javanbakht, A.R. Hassaninejad, H. Sharghi, M.R. Ganjali, M. F. Mousavi, Electroanalysis 15 (2003) 1251–1259.
[41] J.H. Khorasani, M.K. Amini, H. Motaghi, S. Tangestaninejad, M. Moghadam, Sens. Actuators B 87 (2002) 448–456.
[42] D. Gao, J.-Z. Li, R.-Q. Yu, G.-D. Zheng, Anal. Chem. 66 (1994) 2245–2249.
[43] S. Daunert, S. Wallace, A. Florido, C. Bachas, Anal. Chem. 63 (1991) 1676–1679.
[44] E. Malinowska, J. Niedziolka, M.E. Meyerhoff, Anal. Chim. Acta 432 (2001) 67–78.
[45] E.D. Steinle, U. Schaller, M.E. Meyerhoff, Anal. Sci. 14 (1998) 79–84.