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1 **Study of a novel bisnaphthalimidopropyl polyamine as electroactive**
2 **material for perchlorate-selective potentiometric sensors**

3
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13
14 **Abstract**

15
16 In this work, the new polyamine bisnaphthalimidopropyl-4,4'-diaminodiphenylmethane
17 is proposed as a new ionophore for perchlorate potentiometric sensors. The optimal
18 formulation for the membrane comprised of 12 mmol kg⁻¹ of the ionophore, and 68%
19 (w/w) of 2-nitrophenyl phenyl ether as plasticizer and 31% (w/w) of high molecular
20 weight PVC. The sensors were soaked in water for a week to allow leakage of anionic
21 impurities and for one day in a perchlorate solution (10⁻⁴ mol L⁻¹) to improve
22 reproducibility due to its first usage. The stability constant for the ionophore-perchlorate
23 association in the membrane, $\log \beta_{IL1} = 3.18 \pm 0.04$, ensured a performance
24 characterized by the slope of 54.1(±0.7) mV dec⁻¹ to perchlorate solutions with
25 concentrations between 1.24x10⁻⁷ and 1.00x10⁻³ mol L⁻¹. The sensors are insensitive to
26 pH between 3.5 to 11.0, they have a practical detection limit of 7.66(±0.42) x10⁻⁸ mol L⁻¹
27 ¹ and a response time below 60 s for solutions with perchlorate concentrations above
28 5x10⁻⁶ mol L⁻¹. The accuracy of the results was confirmed by the analysis of the
29 contaminant in a certified reference water sample.

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Key words: Bisnaphthalimidopropyl polyamine, potentiometry, sensors, perchlorate, waters.

1. Introduction

Potentiometric sensors based on carefully designed of permeable lipophilic membranes ideally penetrated by the single analyte of interest are among the most well-established and studied sensor technologies. Accordingly, the proposal of a simple and economical bioaffinity-, gas-, ion- and other molecular assessment methods is made on a regular basis. A common feature for these sensors is that analyte recognition takes place chemically by for example bioreceptors, and various synthetic supramolecular receptors, immobilized in the polymeric substrates ^[1]. Anion recognition chemistry has its roots in the 60s around the same time that cation coordination chemistry of crown ethers and cryptands has been published by Pedersen ^[2] and Lehn ^[3], respectively. Meantime, the coordination chemistry of anions has received little attention and it has only been in the last twenty years that sustained effort has been applied to the problems inherent in binding anions ^[4]. Anions play important roles in area of medicine and catalysis. Pollutant anions have been linked to eutrophication of rivers ^[5] and to carcinogenesis ^[6], since it can disrupt hormones production needed for normal health ^[7]. Nevertheless, the design of anion receptors is particularly challenging due to the larger ion radius relatively to cations, by the more complex electrostatic binding interactions, the higher sensitivity to pH variations and the wider range of

58 geometries that requires complementary receptors adjusted to the anionic guest ^[8]. In
59 contrast to cations, only a comparatively small number of anion-selective electrodes
60 are known and their selectivities are often comparatively worse than the cation
61 counterparts ^[9]. Thus, potentiometric sensors for rather lipophilic anions such ClO_4^- ,
62 SCN^- and NO_3^- are usually based on polymeric membranes containing anion
63 exchangers such as lipophilic ammonium salts ^[10].

64 For a number of years special attention has been given to the design and synthesis of
65 analogues/homologues/derivatives of natural polyamines. Some of them have shown
66 promising results concerning to the proliferation of all eukaryotic cells and in the
67 development of novel therapeutic agents ^[11]. Their chemical structures also appear
68 attractive to be exploited in the selective recognition process grounding sensor
69 technologies. In the present work, the newly synthesized bisnaphthalimidopropyl-4,4'-
70 diaminodiphenylmethane (BNIP(4,4)DaDPM)(Figure 1), is evaluated as an ionophore
71 candidate for potentiometric membranes preparation. Several sensors, incorporating a
72 plasticized PVC membrane with BNIP(4,4)DaDPM and different mediator solvents in
73 the presence or absence of additives (cationic or anionic) were prepared and evaluated
74 against some common inorganic and organic ions. The selectivity coefficients clearly
75 indicate that the sensor is selective to ClO_4^- over a number of other organic and
76 inorganic species.

77

78 Figure 1

79

80 Perchlorate ion is both a naturally occurring and chemically produced to be used in
81 solid rocket fuel, fireworks, flares and explosives. It can also be used for bleaching
82 ending and in some fertilizers too. However scientific research indicates that
83 perchlorate ion can have adverse health effects since it can disrupt the ability of the
84 thyroid glands to produce hormones, needed for normal growth and development. Due
85 to some chemical properties like higher solubility and mobility in water and stability,

86 perchlorate can be easily widespread in the environment. Since significant public
87 health concern has recently been raised, this has warranted much attention by the
88 Environment Protection Agency (EPA). Perchlorate is now included in the first, second
89 and third Contaminant Candidate List that were published in the Federal Register ^[12].
90 EPA has therefore decided to regulate the concentration of perchlorate under the Safe
91 Drinking Water Act and has established an Interim Drinking Water Health Advisory
92 committee that recommends the concentration of perchlorate to be $15 \mu\text{g L}^{-1}$ (1.51×10^{-7}
93 mol L^{-1}) in water ^[13]. Concomitantly, the states of Massachusetts and California
94 promulgated their own enforceable standards of 2 and $6 \mu\text{g L}^{-1}$ for perchlorate in
95 drinking water, respectively. Others states have developed advisory levels or health-
96 based goals ranging from 4 to $51 \mu\text{g L}^{-1}$ ^[14]. Several approaches have been considered
97 by the scientific community to develop analytical methodologies where the detection
98 limit allows the determination of perchlorate ion concentration levels recommended by
99 EPA. Recommended methods for the assessment included the ion-chromatography
100 (IC), in-line column concentration/matrix elimination IC with suppressed conductivity
101 detection, IC with electrospray ionization/mass spectrometry (IC/ESI-MS), liquid
102 chromatography/ESI-MS, and HPLC/ESI-MS ^[14]. Nonetheless, the presence of high
103 amounts of other anions such as chloride, sulfate or carbonate may interfere with the
104 determination of perchlorate ^[14] and as such, destabilizing the baseline in the retention
105 time window. Direct interferences problems could also occur such as in direct
106 chromatographic co-elution, concentration dependent co-elution and ionic character
107 displacement. In the majority of published methods a sample preparation, sample
108 clean-up and the identification of possible interferences must be considered ^[15]. Efforts
109 have been made on the synthesis of macrocyclic compounds with better host-guest
110 relationship for different metals in order to provide potentiometric sensors for
111 environmental applications^[16]. Therefore the highly selective and sensitive sensor based
112 on BNIP(4,4)DaDPM proposed in this work provides a successful direct application as

113 evidenced by using certified reference water samples thus providing a simpler and
114 efficient alternative for perchlorate determination.

115

116 **2. Material and Methods**

117

118 *2.1. Reagents and solutions*

119 Analytical grade chemicals were used without further purification unless otherwise
120 stated. All the reagents used in the synthesis of Bisnaphthalimidopropyl-4,4-
121 diaminodiphenylmethane (BNIP(4,4)DaDPM) plus sodium periodate and potassium
122 chlorate were from Sigma-Aldrich.

123 The following chemicals were purchased from Fluka: high molecular weight poly(vinyl
124 chloride) (PVC), 3-octadecanoylimino-7-(diethylamino)-1,2-benzophenoxazine (ETH
125 5294), tetradodecylammonium bromide (TDDABr), potassium tetrakis(4-
126 chlorophenyl)borate (KTPCIPB), 2-fluorophenyl-2-nitrophenyl ether (FNDPE), 2-
127 nitrophenyl phenyl ether (oNPPE), 2-nitrophenyloctyl ether (oNPOE), dibutyl sebacate
128 (DBS), tetrahydrofuran (THF), the acetate, bromide, chloride, nitrate and salicylate
129 sodium salts, ammonium thiocyanate and certified perchlorate IC standard solution
130 (ICS019-100mL). To assess the quality of results provided by the sensor, perchlorate-
131 WP (QC1178-2mL) certified reference material (in accordance with ISO Guide 34:2009
132 and ISO/IEC 17025:2005) was obtained by Fluka.

133 Sodium sulfate, trisodium phosphate dodecahydrate, ammonium fluoride, di-
134 ammonium hydrogen phosphate, potassium iodide and calcium carbonate were from
135 Merck.

136 All aqueous solutions were prepared with doubly deionized Milli-Q water (conductivity
137 $<0.1 \mu\text{S cm}^{-1}$). Perchlorate stock solutions were prepared daily by weighing about
138 0.014 g of reagent into a 100mL volumetric flask followed by dilution to the mark with a
139 0.033 mol L^{-1} sulfate sodium solution acting as ionic adjuster ($I = 0.1 \text{ mol L}^{-1}$). The
140 calibrating working solutions were prepared from the stock by further dilution.

141 The certified reference material, water sample supplied in 2 mL ampoules, was
142 prepared according the respective certificate of analysis. To a 1000 mL volumetric flask
143 partially filled with doubly deionized water, 1 mL of the certified reference material were
144 added, and the flask was made up to the mark with deionized water.

145

146 *2.2. Apparatus*

147 Potential readings were performed at 25° C with a Crison 2002 micropH digital meter
148 (sensitivity ± 0.1 mV) coupled to an Orion 605 electrode switcher to allow simultaneous
149 evaluation of the electrodes. An Orion 90-02-00, silver chloride/silver double junction
150 electrode with its external compartment filled with a 10% (w/v) of KNO_3 solution
151 (Thermo Orion 900003) was used as reference electrode.

152 pH measurements were performed with a Phillips GAH 110 combined glass electrode.

153 The absorption spectra of the membranes were obtained with a double-beam
154 spectrophotometer Jasco V-660 (Easton, UK) equipped with 2.5 mL disposable UV
155 grade acrylic cuvettes, 10 mm optical path.

156

157 *2.3. Preparation of Ion selective electrodes*

158 Different PVC membranes were prepared by mixing the plasticizer and the additive in
159 mmol % proportions as shown in Table 1. The ionophore concentration was fixed at 12
160 mmol Kg^{-1} (corresponding to 1% (w/w)). Membranes with lower concentrations in the
161 ionophore showed inferior slopes and limited linear ranges of response. Each sensor
162 mixture was then added to PVC previously dissolved in THF (6 mL) and finally dropped
163 over the conductive surface of the sensor body. This conductive surface was made up
164 with a mixture of epoxy resin (Araldite M) with graphite powder following the procedure
165 described earlier^[17]. To allow THF evaporation, the freshly prepared sensors were left
166 in an aerated area at room temperature for 24h.

167 The sensors were soaked in deionized water for one week before their first use and for
168 30 minutes to promote membrane hydration between usages.

169

170 Table1

171

172

173 2.4. Procedures

174 The IUPAC recommendations were followed in the characterization of the sensors ^[18].

175 Accordingly, the electrochemical potential of the cell was determined by adjusting the
176 perchlorate solutions at concentrations ranging from 8×10^{-9} up to 1×10^{-2} mol L⁻¹ after
177 stabilization to ± 0.2 mV. The use of the ionic strength adjuster ensured a contribution
178 of the liquid junction potentials always inferior to 0.6 mV as calculated by means of the
179 Henderson approximation ^[19]. The effect of pH on two perchlorate solutions with
180 different concentrations ($V=200$ mL, 1×10^{-4} and 1×10^{-3} mol L⁻¹) was carried out
181 through small volume additions of either concentrated sulfuric acid or saturated sodium
182 hydroxide solution.

183 The potentiometric selectivity coefficients for most common anions presented in
184 sample matrix were assessed by means of fixed interference method ^[20]: volumes of
185 perchlorate solution were added to solutions containing either 1×10^{-3} or 1×10^{-4} mol
186 L⁻¹ of each interfering ion and the resulting potential recorded. The values obtained
187 were plotted vs. the logarithm of the activity of the perchlorate, the linear portions of the
188 plot were extrapolated and the abscissa of the intersection point was used as
189 numerator in the equation 1 (where z_b is the valence of the interfering ion):

$$190 \quad K_{ClO_4^-, Interf}^{Pot} = \frac{a_{ClO_4^-}}{a_{Interf}^{(-1/z_{Interf})}}. \quad (1)$$

191 The reproducibility of the measurements was estimated by the standard deviation of
192 the potential readings obtained from three perchlorate solutions with concentrations in
193 the range of 1×10^{-6} and 1×10^{-4} mol L⁻¹, and washing the membrane with water between
194 immersions. The time needed to achieve steady potential responses (± 1 mV)
195 (response time of the sensors) after sequential addition of adequate volumes of more

196 concentrated perchlorate solutions to the ionic adjuster solution (sodium sulfate; 0.033
197 mol L⁻¹) was evaluated by connecting a x-t strip chart recorder to the digital meter.
198 The practical detection limit was according the recommendations for nomenclature of
199 ion-selective electrodes ^[18].
200 Prior to analysis, the ionic strength of the sample was adjusted to I=0.1 mol L⁻¹ with
201 sodium sulfate. Suitable aliquots were analyzed and the results extracted from the
202 corresponding calibration plots.

203

204 **3. Results and discussion**

205

206 *3.1. Optimization of the membrane formulation*

207 Potentiometric ion-selective sensors are known for their usefulness in their perm-
208 selective extraction of a preferred ion onto the membrane. This process generates
209 across the interface, a potential difference that has been thoroughly explained by
210 thermodynamic and kinetic approaches ^[21]. The selectivity of the electrode is attributed
211 to the ionophore solubilized in the membrane plasticizer, a compound whose chemical
212 reactivity prevails over the general partition mechanisms dictating solvent extraction of
213 other interfering ions. By acting as complexing agent the ionophore assists in the ion
214 transfer through a reversible mechanism of association/dissociation reaction, which
215 seems to be the case with the bisnaphthalimidopropyl polyamine derivative,
216 BNIP(4,4)DaDPM. The latter is readily soluble in lipophilic solvents, so no significant
217 leakage into the sample aqueous matrix is observed. Its evaluation as an ionophore
218 component in membranes formulated with 12 mmol kg⁻¹ concentration, 68%(w/w) of
219 oNPPE and 31%(w/w) of PVC (Type I, Table 1) is briefly described in Table 2. Each
220 freshly prepared sensor was placed in contact with a range of different inorganic and
221 organic anions. No Nernstian response was obtained for acetate, bromide, chloride,
222 fluoride, hydrogen phosphate, nitrate, phosphate and sulfate for solutions with
223 concentrations below 10⁻³ mol L⁻¹. The presence of the ionophore in the sensor

224 exhibited no difference to those ions and they were further discriminated by both the
225 respective high free hydration energies ^[22] and by the electrostatic repulsion forces
226 caused by anionic impurities of the PVC membrane ^[23]. However, for chlorate, iodide,
227 perchlorate, periodate, salicylate and thiocyanate anions near-Nernstian responses
228 were obtained. Within the latter group of anions, perchlorate demonstrated the lowest
229 detection limit of $7.66 \times 10^{-8} \text{ mol L}^{-1}$ while the highest was registered for chlorate ion
230 ($3.93 \times 10^{-5} \text{ mol L}^{-1}$) (Table 2).

231

232

233 Table 2

234 Similar response trends were also obtained within this set of anions when the influence
235 of the plasticizer was evaluated. A good plasticizer should exhibit sufficient lipophilicity
236 to prevent the ionophore leakage into the sample solution and should not be
237 susceptible to crystallization in the membrane phase ^[24]. It was further shown that
238 careful selection of the plasticizer could enhance the preference of carrier-based ion-
239 selective electrodes to divalent ions over monovalent ions of the same radius thus
240 improving selectivity ^[25]. The membrane described above for the screening of different
241 anions was based on the use of 68% of oNPPE as plasticizer. Membranes with high
242 amount of plasticizer have optimum physical properties and ensure relatively high
243 mobility to their constituents. Thus, the amount of plasticizer to be used in the
244 membranes was kept constant, while assessing the influence of plasticizers with
245 different dielectric constants, respectively FNDPE ($\epsilon=50$), oNPPE ($\epsilon=24.0$), oNPOE
246 ($\epsilon=23.9$) and DBS ($\epsilon=5.4$) (membranes I to IV, Table 1).

247

248 Figure 2

249

250 The calibrations performed with perchlorate solutions show a marked influence in the
251 potentiometric response of the plasticizer used in the sensors membrane (Fig. 2). On
252 one side the very lipophilic dibutyl sebacate appears to impair any interaction between
253 the ionophore and the ClO_4^- . On the other hand, the presence of the higher hydrophilic
254 FNDPE plasticizer resulted in a weaker interaction with the ionophore. However the
255 use of oNPOE leads to the improvement of the linear response range that was only
256 surpassed by the use of the oNPPE. The potentiometric response of the latter is linear
257 for very low concentrations, especially when comparing other perchlorate selective
258 electrodes (Table 3). The strong influence of the plasticizer in the measuring range was
259 also noticed by other workers. Lizondo-Sabater ^[26] reported a study using a polyamine
260 where the replacement of the DBP by the oNPOE improved the low limit of linear range
261 but no simple correlations were found with the polarity alone. In turn, the observed

262 difference in the response between sensors based on oNPOE and oNPPE could be
263 assigned to anionic impurities, mainly the polymer bound ROSO_3^- , RSO_3^- and RCO_2^- ,
264 introduced by the membrane components [23]. Gyurcsányi and Lindner proposed a
265 simple spectrophotometric approach to quantify anionic impurities by means of
266 membranes prepared with a PVC to plasticizer ratio of 1:1 or 2:1 and 0.03 to
267 0.1%(w/w) in the chromoionophore ETH 5294 [27]. The absorbance values of the
268 protonated and deprotonated forms of the chromoionophore are measured after
269 soaking the membranes in acidic and basic solutions. The concentration of anionic
270 sites, C_{sites^-} , is then calculated by means of the equation 2:

$$271 \quad C_{\text{sites}^-} = C_{\text{tot}} \left(\frac{A_p \times f}{\frac{A_p}{f} + A_{up}} \right) \quad (2)$$

272 where C_{tot} is the chromoionophore concentration in the membrane; A_p and A_{up} the
273 absorbance values at 660 nm and 535 nm, respectively. The constant f is the ratio of
274 the molar absorption coefficients at the two wavelengths ($f = \epsilon_{up} / \epsilon_p$). Two membranes
275 prepared with 1.18 PVC/oNPOE(w/w) and 1.15 PVC/oNPPE(w/w) with respectively
276 $0.56 \text{ mmol kg}^{-1}$ and $0.64 \text{ mmol kg}^{-1}$ in the chromoionophore were casted with matched
277 thickness upon the wall of two acrylic optical cuvettes and the ionic sites concentration
278 assessed experimentally. After a week of hydration the color of the membranes
279 gradually changed from dark blue to pink. The amount of determined anionic impurities
280 also decreased to the final constant value of $0.14 \text{ mmol kg}^{-1}$ for the membrane
281 prepared with the oNPOE and to the amount of $0.09 \text{ mmol kg}^{-1}$ for the membrane
282 prepared with the oNPPE (Fig. 3). The respective f values of 0.83 and 3.07 were used
283 in the equation 2. These results enabled us to conclude that the response at low
284 perchlorate concentrations of observed for the sensors prepared with the oNPPE could
285 be partly explained by the lower repulsion between the impurity charges in the
286 membrane and the analyte ions. In fact, the membranes formulated with
287 BNIP(4,4)DaDPM and containing the anionic additive KTpCIPB (Table 1, membranes
288 V) were irresponsive. The additional negative sites provided by the tetraphenylborate

289 anion diminished the extraction of perchlorate by the same electrostatic repelling
290 mechanism. The presence of additive probably induced a charge imbalance of the
291 membrane evidenced by the negative values of the electromotive forces generated by
292 the potentiometric cell when compared with the remaining membranes and a slight
293 positive response noticed with the increase of the analyte concentration. In turn, the
294 sensors obtained after the incorporation of cationic sites in the selective membrane
295 gave responses with a sigmoid pattern (Table 1, membranes VI and VII). First, they
296 show no response for ClO_4^- concentrations below $10^{-6} \text{ mol L}^{-1}$. Then a super-Nernstian
297 response is attained for almost one concentration decade and finally a Nernstian
298 response is observed. A similar shaped curve was however obtained for higher
299 concentrations for the sensor with higher concentration of cationic additive (Table 1,
300 membrane VII). The results suggest that the cationic additive induced an extra ion-
301 exchange mechanism responsible for the depletion of perchlorate ions at the
302 membrane interface and for a flux of exchange with interfering ions in the sample side
303 evidenced by the super-Nernstian behavior ^[28]. This behaviour is not new and was
304 already observed for several alkyl-polyamines. M. Jesus Segui and co-workers ^[29], put
305 in evidence that while the polyamines studied were added to the selective membrane in
306 their neutral form, anionic response was achieved without the addition of ionic sites.
307 The rationale for the response was that previous soaking in aqueous solution of the
308 analyte provided membrane stabilization and simultaneously accomplished partial
309 protonation of the ionophore at the membrane interface. In accordance,
310 BNIP(4,4)DaDPM interacts with anions via electrostatic forces when the amines are
311 partially protonated, or via hydrogen bonding.

312

313 Figure 3

314

315 Mikhelson^[30] showed that the determination of the stability constants of the complex
316 ion-ionophore in the hydrophobic matrix of the membrane is feasible through evaluation

317 of the difference of potentials between two membranes, prepared with and without the
 318 ionophore, and in contact with the same solution of the analyte. For any ion-selective
 319 electrodes with inner internal solution configuration the potential E_M of the selective
 320 membrane is given by the potentials of the two membrane-aqueous phase boundaries
 321 according the equation (3):

$$E_M = \frac{RT}{z_i F} \ln \frac{a_i(aq)' a_i(org)''}{a_i(org)' a_i(aq)''} \quad (3)$$

322 where a_i refers to the main ion activity in aqueous (aq) and of its free form in organic
 323 (org) phases at the sample (') and inner solution side (')' respectively (the charge of
 324 the main ion is z_i , and the constants R,T and F have their usual meaning). The activity
 325 of the free ion in the organic phase is constant but higher or lower according the extent
 326 of ion-pairing with the additive sites in the membrane and the stability constant β_{ILn} of
 327 the ion-ionophore complex. From the experimental assay of the two freshly prepared
 328 membranes, one with the ionophore and the other without, juxtaposed in the same
 329 electrode configuration, the activity of the free ion $a_i(org)'$ and $a_i(org)''$ become
 330 different and experimental values of β_{ILn} could be then calculated from (4):

$$\beta_{ILn} = (L_T - \frac{nR_T}{z_i})^{-n} \exp\left(\frac{E_M z_i F}{RT}\right) \quad (4)$$

331 in which L_T and R_T represent namely the ionophore and ionic sites concentration and n
 332 the complex stoichiometry. This equation is only valid if the ion-pairing between the
 333 main-ion and the ionic sites in the membrane is negligible which seems to be the case
 334 of the perchlorate sensors described herein where 0.09 mmol kg⁻¹ of anionic impurities
 335 were determined. Several sensors based on PVC membranes only having the oNPPE
 336 as plasticizer but without the polyamine derivative BNIP(4,4)DaDPM were prepared
 337 and soaked in water for one week before used. Three of them, showed potential
 338 differences below 2 mV and were immersed in perchlorate solutions together with other
 339 three perchlorate sensors with the Type 1 membrane and their responses compared.
 340 The sensors without ionophore only provided Nernstian response to perchlorate for
 341 concentrations higher than 2x10⁻⁵ mol L⁻¹. By assuming that the potential developed at

342 the interface contact between the membrane and the conductive support is matched for
343 both kinds of sensors, the difference between the potential values obtained for
344 perchlorate solutions with concentrations of 10^{-4} to 10^{-2} mol L⁻¹ enabled to obtain the
345 $\log \beta_{IL1} = 3.18 \pm 0.04$. This result shows that the better response of the Type I sensor is
346 due to a lower activity of the free ion in the membrane.

347

348 3.2. General characteristics of the ClO_4^- selective sensor

349 After performing successive calibrations and considering both the linear and non-linear
350 response regions of the perchlorate sensor (between 8×10^{-9} and 1×10^{-2} mol L⁻¹), it was
351 clear that the sensors exhibited some drift of potential during the first evaluations due
352 to the low concentration level of perchlorate in the membrane. By trial and error it was
353 concluded that an overnight conditioning period was needed with the sensors soaked
354 in a ClO_4^- 1×10^{-4} mol L⁻¹ solution to improve reproducibility of potentials. Any potential
355 drift was noticed and long term stability of the sensor (more than 3 months) was
356 observed. The lower limits of the linear response, the practical limits of detection, the
357 slopes and the reproducibility were then calculated. According to the results showed
358 previously (table 2) a slope of -54.1 mV dec⁻¹ in the range $(1.24 \pm 0.00) \times 10^{-7}$ -
359 $(1.24 \pm 0.00) \times 10^{-3}$ mol L⁻¹ was obtained with a r^2 of 0.9993. The practical detection limit
360 (PDL) was $(7.66 \pm 0.42) \times 10^{-8}$ mol L⁻¹. The reproducibility between calibrations along a
361 full week was ± 0.7 mV and between electrodes was ± 1.3 mV. The response time,
362 defined as the time which provides a signal corresponding to 95% of the total change
363 of the potential ^[18] was in this sensor clearly dependent of the perchlorate concentration
364 level. Figure 4 shows the response time behavior during a calibration plot.

365

366

367 Figure 4

368

369 The response of the sensors to the pH of sample was evaluated over the pH range
370 between 2 and 12 at two different concentration levels of ClO_4^- . An operation plateau
371 was registered at pH interval of 3.5 to 11.0 (Fig 5). The slight potential increase
372 registered for pH values higher than 11 could be either due to the co-extraction of the
373 NaClO_4 salt leading to perm-selectivity failure or analyte conversion into chloride ions.
374

375 Figure 5

376 The selectivity pattern of the sensor was established both by the fixed interference
377 method. Nernstian responses were obtained for periodate, thiocyanate, iodide,
378 chlorate, hydrogenophosphate and bicarbonate ions. In accordance with Bakker et
379 al. [31] the corresponding thermodynamic $\log K^{\text{Pot}}_{\text{ClO}_4^-, \text{J}}$ could be established by the ratio
380 of the difference between the standard potentials of the interfering ion and perchlorate
381 by the slope of the calibration curve for this last ion. For nitrate, bromide, acetate,
382 chloride and fluoride sub-Nernstian responses were obtained and therefore the fixed
383 interference method was applied to achieve minimum selectivity values. The values of
384 $\log K^{\text{Pot}}_{\text{ClO}_4^-, \text{J}}$ obtained for the proposed sensor are shown in Table 3.

385 As can be seen, the resulting sensor exhibits high preference for perchlorate over
386 lipophilic inorganic anions (thiocyanate, iodide, chlorate, etc.) and biological organic
387 anion like acetate. For sensors based exclusively on ion-exchangers, anions should
388 interfere in the proportion of their free energy of hydration (commonly referred as
389 lyotropic Hofmeister series ($\text{ClO}_4^- > \text{SCN}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{HCO}_3^- > \text{CH}_3\text{COO}^-$),
390 which is not the present case: $\text{ClO}_4^- > \text{I}^- > \text{SCN}^- > \text{CH}_3\text{COO}^- > \text{Br}^- > \text{HCO}_3^- > \text{NO}_3^- > \text{Cl}^-$.

391 Such behaviour clearly indicates that in addition to electrostatic forces leading to the
392 ion pairing, steric hindrance determine better conformation stability for the ion-pair
393 formed with perchlorate. A second conclusion is that the chemical interaction between
394 the BNIP(4,4)DaDPM and anions prevails over the partition of ions between the sample
395 and the membrane according their lipophilic character. Minimal response to sulfate,
396 bicarbonate, chloride, fluoride, nitrate and iodide ions makes the new electrode

397 potentially useful for estimating perchlorate levels in water samples in regions where
398 contaminant is persistent due to industrial sites and in other places where its presence
399 cannot be related with any human activity.

400

401 Table 3

402

403

404 The developed sensor presents lower selectivity to periodate with $K_{ClO_4}^{Pot}$ of -0.58 for
405 perchlorate at 10^{-4} mol L⁻¹ concentrations. In addition the coefficients are smaller than
406 the ones reported by other authors for perchlorate electrodes [32]. On the other hand,
407 periodate is only present in environmental samples in specific cases, not compromising
408 the application of the proposed sensor.

409 The first electrode proposed for perchlorate was patented in 1968 by Ross [33]. Since
410 that time several selective electrodes were developed based on ion association
411 complexes [32a, 34], organic dyes [35], quaternary ammonium salts [32b, 36], metal
412 complexes [32c, 37], polyamines [26], macrocyclic ethers [38], calixarenes [39] and
413 porphyrins [40]. The majority of these electrodes were constructed by adopting
414 configurations with an internal reference solution. However, the elimination of the inner
415 reference solution by direct application of the membrane over a conductive surface,
416 associated with the use a high selective ionophore compound and suitable plasticizers,
417 results in perchlorate selective sensors with good reproducibility and stability [32b, 38].

418 The construction of a perchlorate selective chemical field-effect transistor
419 (CHEMFET) [38a] and MEMFET [38b] has also been reported, as the use of an
420 operational amplifier to sum the potentials supplied by four membranes (ESOA) [32b].
421 These approaches did not result in an improvement of the main characteristics,
422 especially in the selectivity and detection limit but affected the determination of reduced
423 concentrations in the environmental samples. Furthermore only some of the reported
424 electrodes were applied to real samples, such as water and urine (Table 4). The herein

425 proposed sensor is of simpler implementation when compared with inner solution
426 based ISEs described in the Table 4, which make it as a good candidate for coupling to
427 automatic methods in different configurations. Apart from providing an analytical
428 response to very low concentration levels of ClO_4^- (one decade concentration better
429 regarding the practical detection limit and the lower limit of linear range) it also shows a
430 high selectivity against the main interference in water samples, enabling the use in
431 environmental analysis. To justify such analytical utility, the analysis of a sample of
432 certified water containing perchlorate was considered.

433

434

435 Table 4

436 In the application three sensor units were used and measurements were made in
437 triplicate. The perchlorate concentrations of 52.2 ± 7.6 , 48.7 ± 7.3 and $54.4 \pm 6.3 \mu\text{g L}^{-1}$
438 were respectively measured in certified water sample. These results are in accordance
439 with the certified value of the sample ($45.5 \pm 0.232 \mu\text{g}$, gravimetric), with an acceptance
440 limits between 36.4 and 54.6, since the experimental t values of 1.52, 0.739 and 2.42
441 are below the tabled t value of 4.302 for 95% confidence level. In table 3, the
442 concentrations of the studied interfering ions that would produce a determination error
443 of 3% on the certified value of the sample are presented. These values were calculated
444 from equation (5) [20]:

$$445 \quad C_j^{-1/z_j} = \frac{4.57 \times 10^{-7}}{K_{i,j}} \left(\frac{3}{100} \right)^{-1/z_j} \quad (5)$$

446 where C_j is the concentration of the interfering ion causing the error level before stated,
447 z_j is its valence charge, $K_{i,j}$ is the selectivity coefficient. The numerator of the first factor
448 on the right corresponds to the concentration stated for the certified sample in mol L^{-1} .
449 According to EPA, the maximum contaminant levels for fluoride and nitrates are
450 respectively 4 mg L^{-1} and 10 mg L^{-1} , slightly above the calculated values in Table 3,
451 which could explain the positive shift of the values determined experimentally.

452

453 **4. Conclusions**

454

455 In this work the use of a bisnaphthalimidopropyl polyamine, BNIP(4,4)DaDPM allowed
456 the development of simple potentiometric selective sensors with sensitivity and
457 selectivity enough to provide direct measurement of perchlorate as water contaminant
458 at permissible levels stated by the regulation authorities. The correct response of the
459 sensors is confirmed by the selective extraction into the sensors membrane of
460 perchlorate ions, promoted by the polyamine derivative. The equilibrium established in
461 the membrane between the perchlorate and the polyamine-perchlorate complex not
462 only ensure a low amount of the free ion responsible for the Nernstian response

463 observed at low concentrations but also enables the improved selectivity due the
464 charge repelling promoted by the anionic impurities usually associated with the PVC
465 membranes.

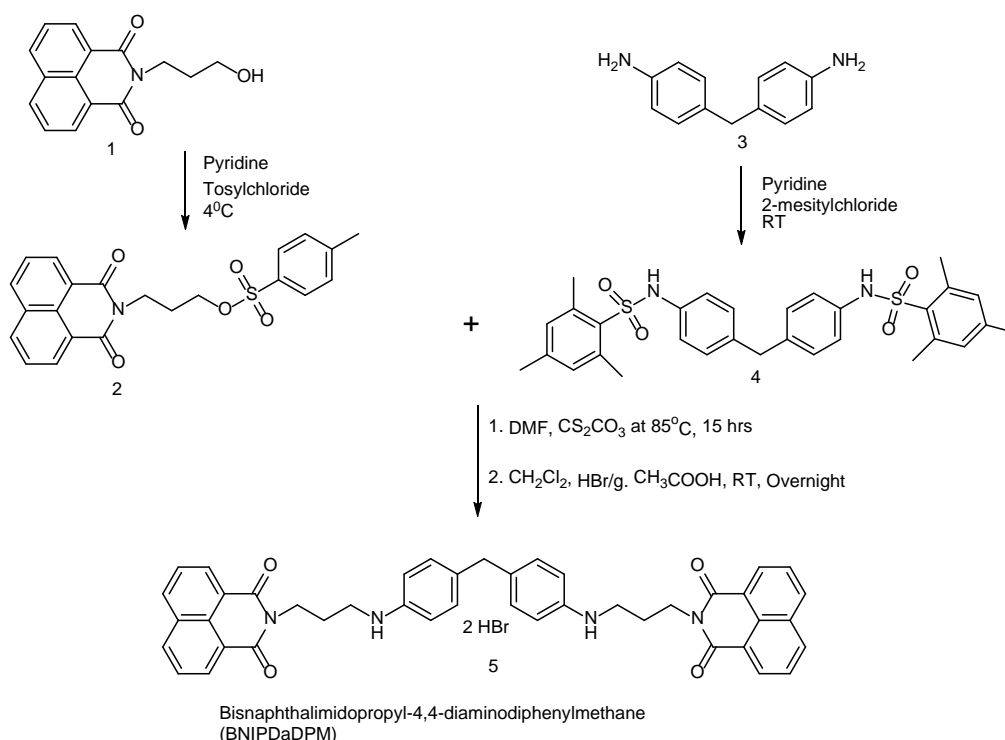
466

467 **Appendix**

468

469 Synthesis and characterization of Bisnaphthalimidopropyl-4,4-diaminodiphenylmethane

470 (BNIP(4.4)DaDPM)



471

472 Naphthalimidopropanol **1** was synthesised as described in our previous publication ^[41].

473 Synthesis of Toluenesulfonyloxypropyl naphthalimide **2**

474 In a 250mL round bottomed flask, hydroxypropyl naphthalimide **1** (5.00g, 0.0196 mol)
475 was dissolved in anhydrous pyridine (80mL). The solution was stirred for 15 minutes at
476 0°C (on ice), then 5.61g of Toluenesulfonyl chloride (Ts-Cl) (0.0294 mol) was added
477 slowly, over 30 minutes. The reaction was left in the fridge overnight at 4°C. When the
478 reaction was complete, the solution was poured into 200mL of icy water, stirred with a
479 glass rod and left to settle for 30 minutes to form a precipitate. The precipitate was

480 filtered off and washed thoroughly with water. The precipitate dried under vacuum at
481 50°C overnight. The crude product was recrystallised from ethanol to give
482 toluenesulfonyloxypropylnaphthalimide (67% yield) **2**.

483

484 ¹H NMR (CDCl₃): δ 8.6–7.3 (aromatic protons), 4.2 (4H, CH₂-O, CH₂-N), 2.4 (3H,
485 CH₃), 2.2 (2H,CH₂)

486 Synthesis of N,N-bismesityl-4,4-diaminodiphenylmethane **4**

487 In a round bottomed flask, 4,4-diaminodiphenylmethane (2.27g, 0.01145 mol) was
488 dissolved of anhydrous pyridine (35 mL). The solution was stirred at 0°C (on ice) until
489 fully dissolved, then Mesityl-Cl (5.26g, 0.02404 mol, 2.1 x excess) was added slowly,
490 over 15 minutes. The reaction was stirred for 1 hour at 0°C (on ice). After the reaction
491 was completed, the solution was poured into 50mL of icy water while stirring and left to
492 settle for 15 minutes to form a precipitate. The precipitate was filtered off and was
493 thoroughly washed with water. The precipitate was dried under vacuum at 50°C for 2
494 hours. Once dried, the crude product was recrystallised from ethanol to give N,N-
495 bismesityl-4,4-diaminodiphenylmethane (**4**) (42% yield). ¹H NMR (CDCl₃) δ: 7.40-6.70
496 (aromatic protons), 5.0 (broad, 1H, NH), 3.90 (2H, -CH₂-), 2.70 (12H, 4 xCH₃), 2.50
497 (6H, 2 x CH₃).

498 Synthesis of Bisnaphthalimidopropyl-4,4-diaminodiphenylmethane (BNIPDaDPM, **5**)

499 In a round bottomed flask (50mL), 0.3g of **4** (0.47 mmol) and 0.39g of **2** (0.945 mmol,
500 2.01 x excess) was dissolved in DMF (8mL). Once fully dissolved, 0.766g of Cesium
501 Carbonate (2.35 mmol) was added slowly, over 20 minutes. The solution was stirred for
502 96 hrs at 60°C. When the reaction was complete, the solution was poured into 50mL of
503 icy water and stirred with a glass rod until a precipitate formed. The latter was filtered
504 off, washed thoroughly with water followed by ethanol and subsequent drying under
505 vacuum at 50°C for 2 hours (80% yield). ¹H NMR (CDCl₃) δ: 8.60-7.07 (Naphthalimido
506 protons), 6.81 (Mesityl aromatic protons), 4.18 (4H, triplet, -CH₂-), 3.93 (2H, singlet, -

507 CH₂-), 3.77 (4H, triplet, 2 x -CH₂-), 2.46 (12H, singlet, 4 x CH₃), 2.22 (6H, singlet, 2 x
508 CH₃), 1.89 (4H, pentet, 2 x -CH₂-).

509

510 HRMS (ESI): calculated for C₆₁H₆₀N₅O₈S₂, 1054.3878 [M]⁺. Found 1054.3874.

511

512 In a round bottomed flask, BNIP-bis-Mts-diaminodiphenylmethane (0.34g, 0.330 mmol)
513 was dissolved in 7.5mL of anhydrous dichloromethane (DCM) followed by the addition
514 of 1.2mL of hydrobromic acid in glacial acetic acid (HBr/gCH₃CO₂H). The solution was
515 left stirring for 96 hours at room temperature and monitored using TLC. When
516 completed, a precipitate was formed. The latter was filtered off and washed with 20mL
517 of anhydrous DCM and 15mL of ether. The Bisnaphthalimidopropyl-4,4-
518 diaminodiphenylmethane dihydrobromide salt (BNIPDaDPM, LC-1) (0.2 mmol, 67%
519 yield), was dried under vacuum at 50°C overnight. ¹H NMR (DMSO-d₆) δ:8.50-6.55
520 (Aromatic protons from Naphthalimido and benzenes rings). 4.13 (4H, triplet, -CH₂-),
521 3.64 (2H, -CH₂-), 3.21 (4H, triplet, 2 x -CH₂-), 1.91 (4H, triplet, 2 x -CH₂-).

522

523 HRMS (ESI): calculated for C₄₃H₃₆N₄O₄ 2HBr. 673.2737 [M-2HBr]⁺. Found 673.2796.

524

525

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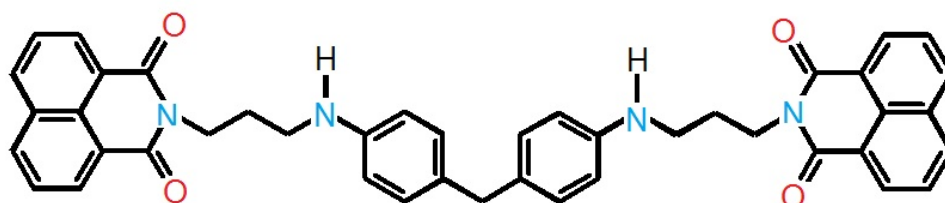
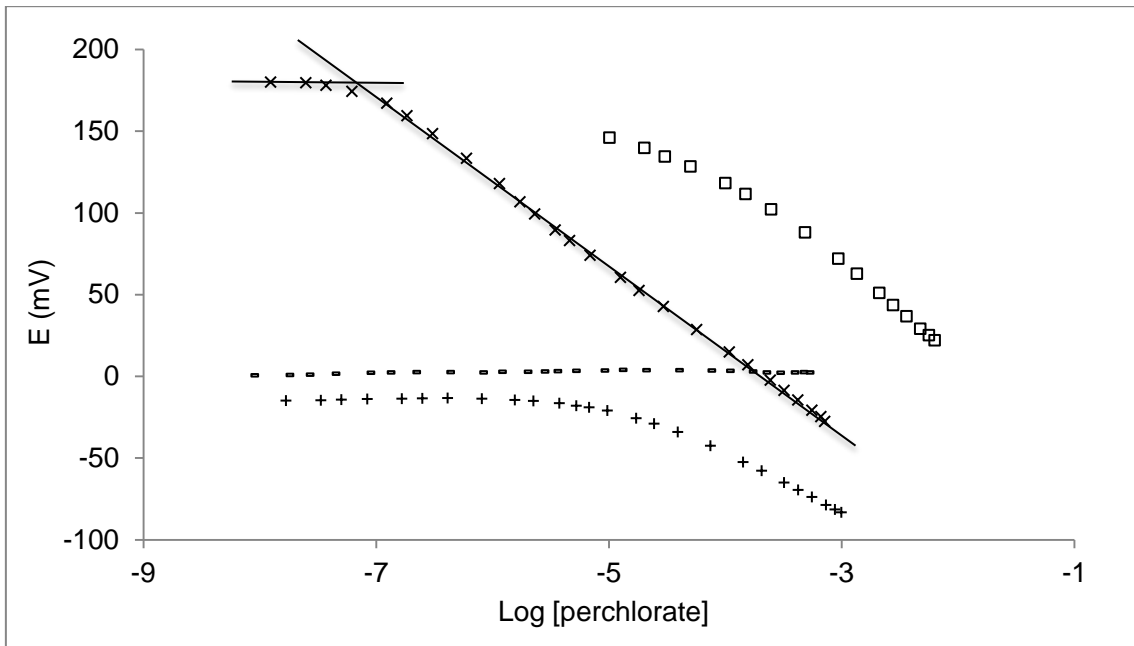


Figure 1: Chemical structure of bisnaphthalimidopropyl-4,4'-diaminodiphenylmethane (BNIP(4,4)DaDPM)

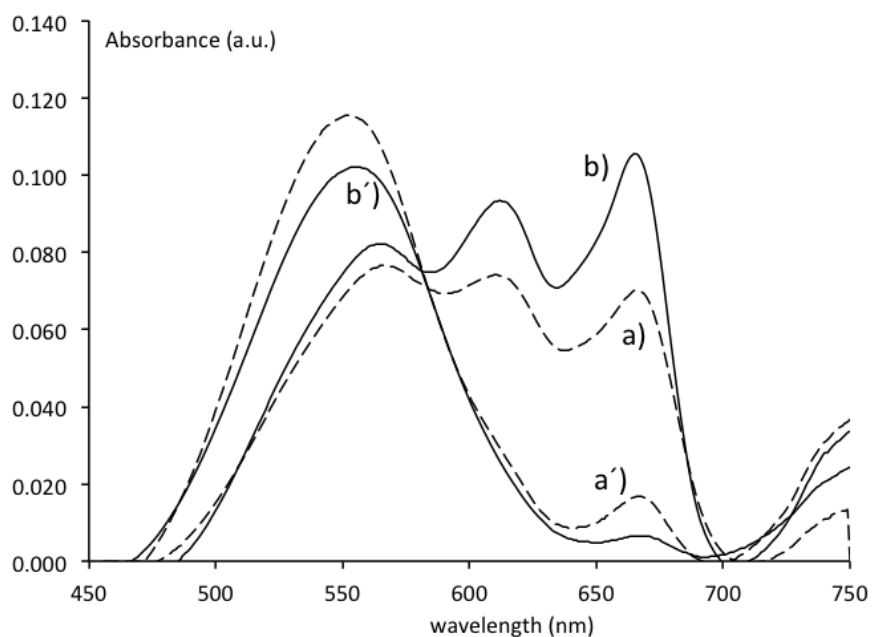
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657 Figure 2: Potentiometric response for the ClO_4^- anion, according to the plasticizer used in
658 the membrane: + 2-fluorophenyl-2-nitrophenyl ether; x 2-nitrophenyl phenyl ether; □ 2-
659 nitrophenyloctyl ether; - dibutyl sebacate.

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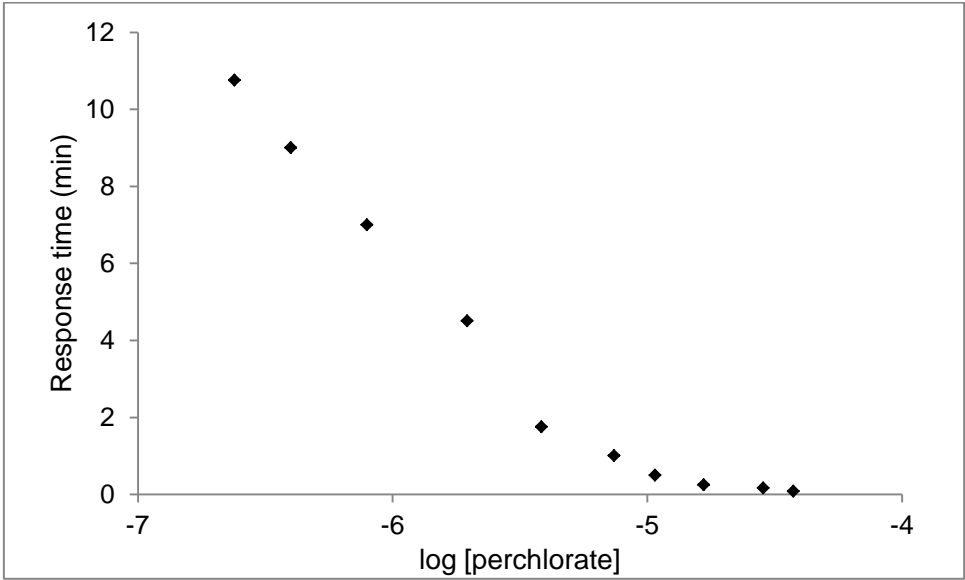
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675 Figure 3: Visible spectra of membranes prepared with oNPOE: a) after two hours
676 period soaked in 0.1 mol L⁻¹ HCl; a') after one week, and with oNPPE: b) after two
677 hours and b') after one week. The bands near 560 and 660 nm correspond
678 respectively to unprotonated and protonated ETH 5294 chromoionophore.
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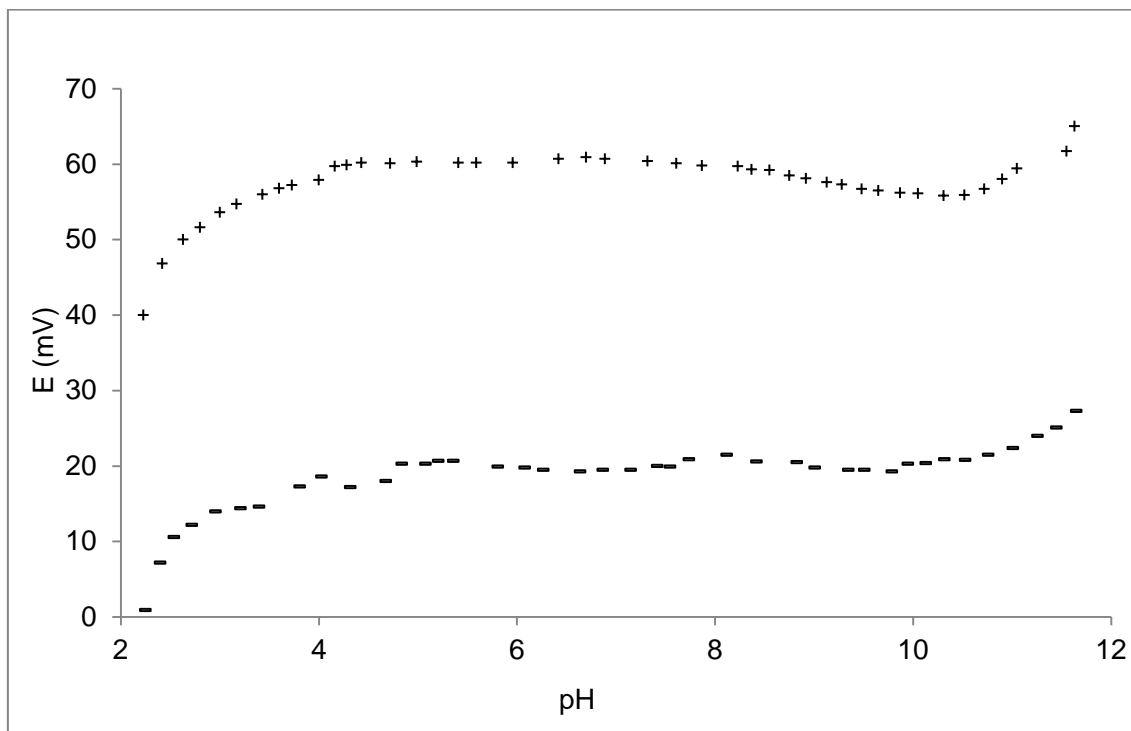
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Figure 4: Response time of the optimized ClO_4^- selective electrode

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Figure 5: The effect of pH on the ClO_4^- selective electrode. (—) $1 \times 10^{-3} \text{ mol L}^{-1}$; (+) $1 \times 10^{-4} \text{ mol L}^{-1}$.

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725 Table 1: Membrane compositions and the main sensor characteristics of the assayed
 726 perchlorate-selective sensors

Membrane composition	I	II	III	IV	V	VI	VII
BNIP (4.4) DaPM (% w/w)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
oNPPE (%w/w)	68.0	-	-	-	68.0	68.0	68.0
oNPOE (%w/w)	-	68.0	-	-	-	-	-
FNDPE (%w/w)	-	-	68.0	-	-	-	-
DBS (%w/w)	-	-	-	68.0	-	-	-
KTpCIPB (mmol %)	-	-	-	-	59.8	-	-
TDDABr (mmol %)	-	-	-	-	-	57.1	25.8
PVC (%w/w)	31.0	31.0	31.0	31.0	31.0	31.0	31.0
Slope (mV dec ⁻¹)	(-54.1) _{n=12}	(-40.1) _{n=6}	(-33.4) _{n=6}	---	---	(-71.2) _{n=6}	(-61.5) _{n=6}
LLLR (mol L ⁻¹)	(1.24x10 ⁻⁷) _{n=12}	(5.05 x10 ⁻⁵) _{n=6}	(5.53x10 ⁻⁶) _{n=6}	---	---	(1.17x10 ⁻⁵) _{n=6}	(8.30x10 ⁻⁵) _{n=6}
PDL (mol L ⁻¹)	(7.66x10 ⁻⁸) _{n=12}	n.d.	(5.17x10 ⁻⁶) _{n=6}	---	---	(1.17x10 ⁻⁵) _{n=6}	(8.30x10 ⁻⁵) _{n=6}

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742 Table 2: Potentiometric responses to different common anions of an ion-potentiometric sensor with a membrane containing 12 mmol kg⁻¹ of
 743 BNIP(4.4)DaDPM, 68%(w/w) of oNPPE and 31%(w/w) of PVC.

Anion	Chlorate	Iodide	Perchlorate	Periodate	Salicylate	Thiocyanate
Slope (mV dec⁻¹)	-55.7	-51.9	-54.1	-57.6	-49.1	-51.5
Reproducibility						
Between calibrations	---	2.0 _{n=3}	0.7 _{n=3}	1.57 _{n=4}	---	2.5 _{n=2}
Between electrodes	0.5 _{n=4}	0.4 _{n=3}	1.3 _{n=3}	0.5 _{n=3}	1.2 _{n=4}	1.6 _{n=3}
R²	0.9992 _{n=4}	0.9978 _{n=9}	0.9993 _{n=9}	0.9988 _{n=12}	0.9964 _{n=4}	0.9987 _{n=6}
LLLR (mol L⁻¹)	(4.11 ± 0.00) × 10 ⁻⁵	(3.26 ± 0.75) × 10 ⁻⁶	(1.24 ± 0.00) × 10 ⁻⁷	(9.08 ± 1.82) × 10 ⁻⁷	(1.97 ± 0.00) × 10 ⁻⁵	(4.11 ± 0.00) × 10 ⁻⁷
PDL (mol L⁻¹)	(3.93 ± 0.19) × 10 ⁻⁵	(1.55 ± 0.17) × 10 ⁻⁶	(7.66 ± 0.42) × 10 ⁻⁸	(6.41 ± 1.76) × 10 ⁻⁷	(1.27 ± 0.03) × 10 ⁻⁵	(2.77 ± 0.34) × 10 ⁻⁷

744 Table 3: Selectivity of the perchlorate sensors relatively to different ions

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Interfering ion	$\log K_{\text{Perchl, Interf}}$	Concentrations (mg L^{-1}) which would introduce an error of 3% error in the certified sample determination
Periodate	-0.58	0.01
Iodide	-1.96	0.13
Chlorate	-2.47	0.34
Salicylate	-2.61	0.77
Thiocyanate	-2.62	0.33
Acetate	-3.33	1.74
Bromide	-3.46	3.96
Bicarbonate	-3.95	7.41
Nitrate	-3.95	7.59
Chloride	-4.10	6.09
Fluoride	-4.11	3.36
Hydrogenophosphate	-4.40	13.95

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Table 4: Comparison of the main characteristics of perchlorate selective electrodes found in the literature

Electrode Type	Ionophore	Lipophylic Salt	Slope (mV dec ⁻¹)	Linear Range (mol L ⁻¹)	PDL (mol L ⁻¹)	Response Time (s)	pH range	Application	Reference
IS: ClO ₄ ⁻ 1x10 ⁻² mol L ⁻¹ ₁	Cu complex	TOMAC	-59.4±0.3	1x10 ⁻⁶ -1x10 ⁻²	4x10 ⁻⁷	9	3 - 10	Tap water	[37b]
IS: ClO ₄ ⁻ 1x10 ⁻¹ mol L ⁻¹ ₁	Co(DBM) ₂	MTOAc	-60.3±0.5	8x10 ⁻⁷ -1x10 ⁻¹	5.6x10 ⁻⁷	< 5	2 - 9	Water. urine	[37c]
IS: ClO ₄ ⁻ 1x10 ⁻¹ mol L ⁻¹ ₁	Ni(DBM) ₂	MTOAc	-60.0±0.8	1x10 ⁻⁶ -1x10 ⁻¹	6.6x10 ⁻⁷	< 5	1.2 – 12.5	Water. urine	[37d]
IS: MES buffer	Calixarene	--	-58	--	1x10 ⁻⁷	--	--	--	[39]
IS: ClO ₄ ⁻ 1x10 ⁻¹ mol L ⁻¹ ₁	Polyamine	--	-52.5	5.5x10 ⁻⁶ – 1x10 ⁻¹	4.2x10 ⁻⁶	3	--	--	[26]
IS: ClO ₄ ⁻ 1x10 ⁻² mol L ⁻¹ ₁	UO ₂ L	HTAB	-60.6	1x10 ⁻⁶ -1x10 ⁰	8x10 ⁻⁷	< 10	3.5 - 12	Water. urine	[42]
IS: ClO ₄ ⁻ 1x10 ⁻² mol L ⁻¹ ₁	Porphyrin	CTAB	57.8±0.4	8.0x10 ⁻⁶ – 1.6x10 ⁻¹	5x10 ⁻⁶	< 10	3.0-9.5	Water. urine	[40]
CGCE			53.6±0.4	1x10 ⁻⁶ – 3x10 ⁻²	7x10 ⁻⁷				
IS: ClO ₄ ⁻ 1x10 ⁻³ mol L ⁻¹ ₁	Ni(II)tetraazamacrocyclic	HTAB	59.3	5x10 ⁻⁷ -1x10 ⁻¹	2x10 ⁻⁷	< 10	3.5 – 11.0	Water. urine	[37a]
IS: ClO ₄ ⁻ 1x10 ⁻¹ mol L ⁻¹ ₁	Cu(II) complex	--	67	--	1.3 x10 ⁻⁵	< 3	3 - 12	--	[37e]
IS: ClO ₄ ⁻ 1x10 ⁻² mol L ⁻¹ ₁	Gold(I) complex	--	-56.77±0.43	5x10 ⁻⁶ – 1x10 ⁻²	1x10 ⁻⁶	< 10	2-12	Water. urine	[32c]
IS: ClO ₄ ⁻ 1x10 ⁻² mol L ⁻¹ ₁	Zn complex	HTAB	58.7±0.3	8.3x10 ⁻⁷ – 1.0x10 ⁻²	5.4x10 ⁻⁷	12	3.0-8.0	Water, Biological samples	[43]
ISE Solid contact			59.3±0.2	1.0x10 ⁻⁷ – 1.0x10 ⁻²	8.4x10 ⁻⁸	9	2.5-9.0		
ISE Solid contact	Ammonium salt	--	-57.3±1.0	8.2x10 ⁻⁶ - -	1.3x10 ⁻⁶	< 15	3.5 - 12	Pyrotechnic mix.	[32b]
ESOA			-255.8±3.8	5.1x10 ⁻⁶ - -	1.2x10 ⁻⁶				

ISE _{Solid contact}	Phosphadithiamacrocycle	--	-54	1×10^{-6} - 1×10^{-2}	8×10^{-7}	< 10	1.5 – 13.5	--	[38b]
MEMFET			54	6×10^{-7} - 1×10^{-2}	3×10^{-7}	< 4	1 - 11		
ISE _{Solid contact}	Phosphadithiamacrocycle	--	-56	1×10^{-6} - 1×10^{-2}	8×10^{-7}	< 10	1.5 – 13.5	--	[38a]
CHEMFET			54	6×10^{-7} - 1×10^{-2}	3×10^{-7}	< 4	1 - 11		

IS- Inner solution; PDL- Practical Detection Limit; CGCE: coated glass carbon electrode; ESOA- Operational amplifier to sum the potentials supplied by four membranes; Ammonium salt : tetraoctylammonium chloride; CTAB: cetyltrimethylammonium bromide; HTAB- hexadecyltrimethylammonium bromide; MTOAc - methyltriethylammonium chloride; TOMAC-trioctylmethyl ammonium chloride; Calixarene: tetra(triphenylphosphonium) p-tert-butylcalix[4]arene 2; Cu complex : [Cu((benzyl)2[16]aneN6)](ClO4-); UO2L: 2.2-[1.2-ethanediyl-bis(nitriloethylidene)]-bis-phenolato uranyl; Cu(II) complex: 1,4,8,11-tetra(n-octyl)-1,4,8,11-tetraazacyclotetradecane perchlorate (I); Gold (I) complex: bis[tri-(p-methoxyphenyl) phosphine] gold(I); Ni(DBM)2 :bis(dibenzoylmethanato) nickel(II); Ni(II)tetraazamacrocyclic: nickel(II)-hexaazacyclotetradecane complexes; Phosphadithiamacrocycle : 7-phenyl-7-phospha-3,11-dithiabicyclo[11,4,0]heptadeca-13(1),14,16-triene; Polyamine : 1,4,8,11-tetra(n-octyl)-1,4,8,11-tetraazacyclotetradecane; Prophyrin: dichlorophosphorous(V)-tetraphenylporphyrin(I); Zinc complex: 6,7:13,14-dibenzo-2,4,9,11-tetramethyl-1,5,8,12-tetramethylacrylate-1,5,8,12-tetraazacyclotetradecane-6,13-diene

1 **Study of a novel bisnaphthalimidopropyl polyamine as electroactive**
2 **material for perchlorate-selective potentiometric sensors**

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15 Figure 1: Chemical structure of bisnaphthalimidopropyl-4,4'-diaminodiphenylmethane
16 (BNIP(4,4)DaDPM)

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18 Figure 2: Potentiometric response for the ClO_4^- anion, according the plasticizer used in
19 the membrane: + 2-fluorophenyl-2-nitrophenyl ether; x 2-nitrophenyl phenyl ether; □ 2-
20 nitrophenyloctyl ether; - dibutyl sebacate.

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22 Figure 3: Visible spectra of membranes prepared with oNPOE: a) after two hours
23 period soaked in 0.1 mol L^{-1} HCl; a') after one week, and with oNPPE: b) after two
24 hours and b') after one week. The bands near 560 and 660 nm correspond
25 respectively to unprotonated and protonated ETH 5294 chromoionophore.

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27 Figure 4: Response time of the optimized ClO_4^- selective electrode

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29 Figure 5: The effect of pH on the ClO_4^- selective electrode. (–) $1 \times 10^{-3} \text{ mol L}^{-1}$; (+) 1×10^{-4}
30 mol L^{-1} .

31 Table 1: Membrane compositions of the assayed perchlorate-selective sensors

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33 Table 2: Potentiometric responses to different common anions of an ion-potentiometric
34 sensor with a membrane containing 12 mmol kg⁻¹ of BNIP(4.4)DaDPM, 68%(w/w) of
35 oNPPE and 31%(w/w) of PVC.

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37 Table 3: Selectivity of the perchlorate sensors relatively to different ions

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39 Table 4: Comparison of the main characteristics of perchlorate selective electrodes
40 found in the literature

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