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Flow-through bulk optode for the fluorimetric determination of perchlorate

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Abstract

A flow-through fluorescence bulk optode for the flow-injection determination of perchlorate is described. As the active constituents the optode incorporates the lipophilized pH indicator fluorescein octadecyl ester and methyl tridodecyl ammonium chloride, dissolved in a plasticized poly (vinyl) chloride membrane entrapped in a cellulose support. The optode is applied in conjunction with the flow injection technique for perchlorate determination at pH 4.5 (acetic–acetate). The sensor is readily regenerated with the pH 10.4 (TRIS) carrier solution. The analytical characteristics of this optode with respect to perchlorate response time, dynamic measurement range, reproducibility and selectivity are discussed. The proposed FI method is applied to the determination of perchlorate in waters from different sources.

Keywords: Flow-through optode; Fluorimetry; Perchlorate; Water

1. Introduction

Optical sensing systems that work on the principle of the analyte being partitioned into the bulk of a plasticized polymeric membrane have been developed for the determination of cations [1–7] and anions [8–17]. Theoretical aspects of the bulk optode membranes have been studied by Seiler and Simon [18].

The membranes contain a lipophilic pH indicator dye, whose absorbance, reflectance or fluorescence is used for optical transductions. In some cases the membrane also contains an ionic additive to provide charged sites and a chromoionophore for the analyte recognition process.

In the case of anion determination, the optical transductions is based on the protonation and deprotonation of the pH indicator dye coupled with the anion concentration through co-extraction or repulsion of the anion/proton pair to and from the membrane. If the membrane contains no ion-selective ionophore, the selectivity of the

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optode membrane depends on the lipophilicity of the anions (Hofmeister series).

In previous papers we described flow-ion sensitive bulk optode membranes that incorporated a metallochromic dye as chromogenic reagent and were applied to determining various metallic ions, in several real samples [19–21].

In this paper, we describe and test the performance of a new flow-through bulk optode for FI-fluorimetric determination of perchlorate. The flow-through bulk optode incorporate the lipophilized fluorescent pH indicator fluorescein octadecylester (FOE) and methyltridodecylammonium chloride (MTDDACl) as the active constituents in a plasticized poly (vinyl) chloride (PVC) membrane entrapped in a cellulose-based support.

As is know the bulk optodes have gained considerably in practical reliability, and can be considered as inexpensive alternatives to certain conventional analytical methods. By changing the membrane composition, an appropriate adjustment of the parameters to a specific set of requirements is possible [18].

The use of chemical sensors in flow-injection analysis considerably simplifies the procedure and may provide higher selectivity than the common photometric/fluorimetric mode of operation. The FI mode of operation automates measurements with the optode membrane and permits the sensor layer of the optode to be regenerated quickly with the same carrier solution. However to our knowledge no FI method for the determination of perchlorate using a flow through bulk optode has been proposed and no optical sensor for the determination of perchlorate has been applied for the determination of this anion in real samples.

Recent research has shown that perchlorate anion may be found at high concentrations ($>$ 1000 mg l^{-1}) in surface waters and groundwaters around the world [22], such contamination mainly being due to the perchlorate salts that are used in a wide variety of industrial situations [23]. Very little is known about the health effects of low-level long-term exposure to perchlorate, such as that which would occur by consuming contaminated drinking water, although it is known that the perchlorate shows thyreostatic activity by inhibiting iodine uptake. It may therefore hinder the ability of humans to produce hormones and regulate their metabolism. Indeed, perchlorate salts have been used to treat patients with hyperactive thyroid glands (Graves' disease) and to carry out diagnostic tests [24]. They have also been used as thyreostatic drugs in cattle fattening and as growth promoters [25].

When the flow-sensor developed in this paper was applied in the FI fluorimetric determination of perchlorate in water from different sources, the results were satisfactory.

2. Experimental

2.1. Apparatus

Fluorimetric measurements were made using an Oriel modular fluorometer (Stratford, USA). A 150-W Xe lamp (model 6255) was powered by an Oriel power supply (model 68805) at 40–200 W. The light from the source passed through the excitation monochromator (model 77250) and was focused on one leg of a fiber optic fluorescence probe (Oriel model 77404). The variable slits (model 77250) on each side of the monochromators were set at 3.16 mm. Light from the monochromator at the excitation wavelength (460 nm) was focused on the sensing membrane and the light emitted from it was directed to the emission monochromator by means of the other leg of the fluorescence probe. The light from the emission monochromator at the selected emission wavelength (539 nm) was carried to the photomultiplier tube (model 70680) powered by a photomultiplier power supply (model 70705). The photomultiplier tube was connected to a transimpedance amplifier (model 70711) which was interfaced with a personal computer via an analog-to-digital converter. A Gilson Minipuls 3 peristaltic pump and Omnifit injection valve were used. A home made flow-through cell similar to that designed by the authors and described previously [19] was used although the new model was refined by constructing the cell with a one 2-mm thick silicon gasket, in the centre of which a 7 mm diameter hole together with two channels of 2×5 mm for the entrance and exit of the flowing solutions had been made. In addition a

silica window instead of a glass window was used in the present flow-through cell. Connecting tubing of 0.5 mm i.d. and various end-fittings and connectors (Omnifit) were used

2.2. Materials and reagents

Poly (vinyl chloride) high molecular mass; bis (2-ethylhexyl) sebacate (DOS); tetrahydrofuran (THF); methyltridodecylammonium chloride (MTDDACl) and fluorescein octadecyl ester ETH 7061 (FOE) (chromoionophore XI) were Selectophore products from Fluka. Filter paper 235 (Albet, Barcelona Spain). The pH buffer solutions were 0.02 M acetate–acetic acid of pH 4.5 and Tris 0.05 M of pH 10.4. All other chemicals were of analytical reagent grade and all solutions were prepared with doubly distilled water.

Stock perchlorate solution (0.1 M) was prepared from $NaClO_4 \cdot H_2O$ and standardized gravimetrically with 1,2,4,6-tetraphenylpyridinium acetate [26]. Working standard solutions of lower concentrations were prepared by suitable dilution with 0.02 M acetate–acetic acid buffer of pH 4.5.

2.3. Optode membrane preparation

The optode was prepared from a coating solution containing 5 mg of FOE, 5 mg of MTDDACl, 50 mg of PVC and 100 mg of DOS dissolved in 3.0 ml of THF. Fifty microliters of this mixture was deposited on a cellulose filter paper (Albet 235). After 1–2 min the THF evaporated and a 5-mm diameter piece was cut out with a cork borer. This was incorporated into the flow-through cell by sticking it on the mirror, with the side on which the mixture had been deposited facing upwards towards the carrier solution. The flow-through cell containing the optode membrane was incorporated in the FI-design selected.

2.4. Manifold and calibration procedure

The manifold used is shown in Fig. 1. To obtain the baseline, a carrier stream of 0.05 M Tris buffer of pH 10.4 was pumped at a flow rate of 1 ml min^{-1}. A volume of 200 μl sample solution

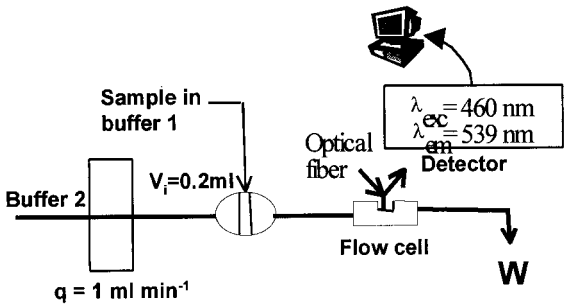


Fig. 1. Flow-injection configuration. Buffer 1: 0.02 M acetate–acetic acid solution pH 4.5. Buffer 2: 0.05 M Tris solution of pH 10.4.

containing 10^{-5}–10^{-3} M ClO_4^- in acetate–acetic buffer solution of pH 4.5 was injected into the carrier and the intensity of fluorescence (λ_{ex} 460 nm, λ_{em} 539 nm) was monitored.

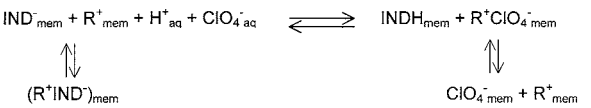
2.5. Procedure for determination of perchlorate in water

No prior treatment of the samples was necessary for the determination of perchlorate in water. The water samples of 20.0 ml were spiked with 100–250 ml of 5×10^{-2} M ClO_4^- solution, 2 ml of 0.25 M acetic–acetate buffer of pH 4.5 were added and diluted with distilled water to 25 ml. The ClO_4^- concentration was determined by applying the recommended FI procedure.

3. Results and discussion

3.1. Principle of operation

The flow-optode membrane contains the fluorescent anionic form of fluorescein octadecyl ester (IND^-_{mem}) and the methyltridodecyl ammonium (R^+_{mem}) as ionic additive. The indicator used is acidic and is not fluorescent in protonated form. The mechanism of the process is:



The degree of protonation of the pH indicator is

dependent on the perchlorate concentration [8], which was determined by buffering the samples at pH 4.5.

3.2. Immobilization of the active constituents

In previous works we found that the highest sensitivity, the best reproducibility and the lowest regeneration times were obtained with a matrix with 2:1 plasticizer/PVC ratio (100/50 mg/mg) dissolved in 3 ml of THF. The best diffusion of the coating solution and wetting were obtained by using Albet 235 filter paper, which was therefore chosen as support. [19]. In this paper the selected plasticizer was bis (2-ethyhexyl)sebacate (DOS), 5 mg of the pH indicator and 5 mg of the ionic additive ammonium quaternary salt provided good results.

3.3. Fluorescence spectrum of the sensor

The excitation and emission spectra of the proposed optode membrane are shown in Fig. 2. The spectra were measured in the FI manifold depicted in Fig. 1 by pumping 0.05 M TRIS solution of pH 10.5 as carrier solution. The maximum bands at λ_{ex} 460 nm, and λ_{em} 539 nm correspond to the deprotonated form of the pH indicator in the membrane and were the wavelengths selected.

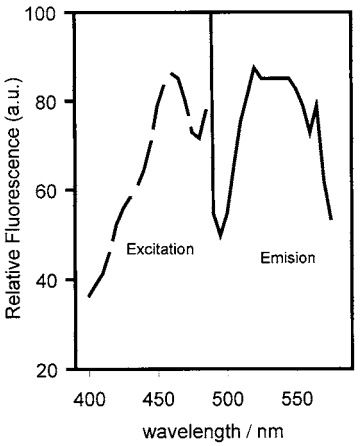


Fig. 2. Excitation–emission spectra of the membrane corresponding to the deprotonated form of the pH indicator.

3.4. Parameters affecting the response

The design of the manifold selected is shown in Fig. 1. Fig. 3 shows the effects of the sample volume, flow rate and pH on the analytical signal. The reactor was kept as short as possible (40 cm) to minimized dispersion.

The description of the response behaviour of this optode is given as an analytical signal $I_R = I_0/I_P$, where I_P corresponds to the fluorescence intensity peak of the sample and I_0 corresponds to fluorescence intensity of the base line.

The volume of injected sample was varied from 40 to 400 μl, the other variables were 1 ml min^{-1} flow rate, 10^{-4} M ClO_4^- at pH 4.5 and carrier solution at pH 10.4. As can be seen in Fig. 3(A), increasing sample volumes increased the sensor response up to 200 μl, which was selected for further studies. Fig. 3(B) shows the influence of the flow rate on the sensor response over the range 0.25–1.20 ml min^{-1} in the same experimental conditions described above. A flow rate of 1.0 ml min^{-1} was selected as a compromise between sensitivity and sample frequency.

The effect of the pH of the sample was studied in the range 4.0–5.8 in the same experimental conditions described above, using Ac^-/HAc buffers. As can be seen in Fig. 3(C) a pH value of 4.5 gave the highest sensor response and this was selected.

3.5. Regeneration of the optode

An eluent to regenerate the optode that can also be used as carrier is best for this type of sensor since the FI procedure is considerably simplified thereby. The best results were obtained using 0.05 M TRIS solution (pH 10.4), which also provided a short membrane regeneration time. The injection rate is determined by this regeneration time, which was found to be dependent on the ClO_4^- concentration.

The lifetime of the membrane optode was at least 1 month in continuous operation.

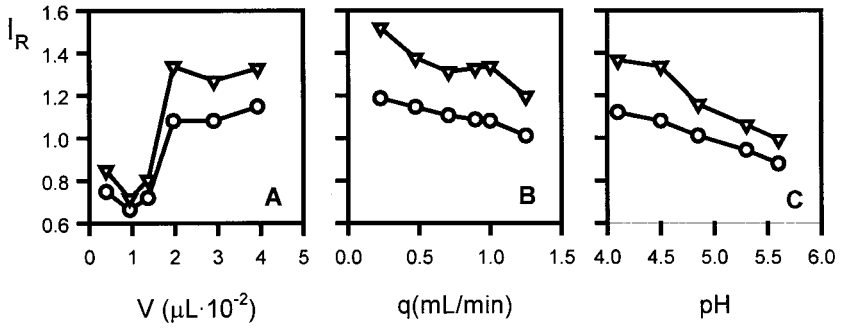


Fig. 3. Effect of (A) sample volume, (B) flow rate and (C) pH on the response: (○) blank; (▽) 1×10^{-4} M perchlorate.

3.6. Response characteristics

The fluorescence response of the optode versus time, in the selected experimental conditions, for different ClO_4^- concentrations in the range 10^{-5}–10^{-3} M is shown in Fig. 4(A). The fluorescence base line, which corresponds to the fluorescence of the optode at pH 10.4 (I_0), was adjusted previously to arbitrary units in the detector. When the ClO_4^- sample plug reached the cell the fluorescence decreased rapidly and continued falling as the sample plug passed through the cell, due to the extraction of the H^+ ClO_4^- pair and the subsequent protonation of the pH indicator in the membrane. Minimum fluorescence was obtained at the very end of the sample zone, after which the TRIS buffer contained in the carrier quickly eluted the H^+ ClO_4^- pair of the optode, making the membrane ready for a new sample.

The corresponding calibration graph obtained by plotting I_R versus log[ClO_4^-] concentration is shown in Fig. 4(B). The experimental date obtained were fitted to a sigmoidal curve of the Gompertz type of three parameters: $I_R = a\ \exp(-\exp-(\log[ClO_4^-]-c)/b)$. The values obtained for the parameters a, b, c and for the correlation coefficient were 0.9056, 0.5068, −3.861 and 0.9993, respectively. The dynamic range of the response toward perchlorate was 5×10^{-5}–1×10^{-3} M ClO_4^-. The limit of detection, calculated as [27], was 3.5×10^{-5} M.

The repeatability of the proposed method was evaluated by performing ten determinations with the 1×10^{-4} M ClO_4^-; the variation coefficient obtained was 3.0%. The variation coefficient of the blank was 1.2%. The between day reproducibility was studied by carrying out the same procedure on five consecutive days with the same membrane, the

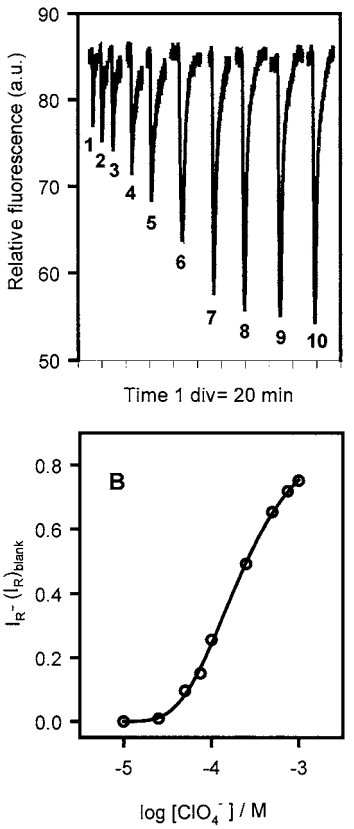


Fig. 4. (A) Intensity fluorescence response to different ClO_4^- concentrations: (1) blank; (2) 1×10^{-5}; (3) 2.5×10^{-5}; (4) 5×10^{-5}; (5) 7.5×10^{-5}; (6) 1×10^{-4}; (7) 2.5×10^{-4}; (8) 5×10^{-4}; (9) 7.5×10^{-4}; (10) 1×10^{-3} M. (B) Plot of $I_R - (I_R)_{blank}$ *vs.* $log[ClO_4^-]$.

Table 1
Anion selectivity coefficients

Anions	log $K_{ClO_4^-,X}$	[X]/M assayed
ClO_4^-	0	–
Cl^-, SO_4^{2-}	< -3.4	10^{-2}
Br^-	-1.9	5×10^{-3}
NO_3^-	-1.4	10^{-3}
I^-	-0.8	10^{-3}

CV for 1×10^{-4} M ClO_4^- was 3.5%. The between membrane reproducibility was evaluated with three membranes from the same coating mixture, the CV for 1×10^{-4} M ClO_4^- (three determinations) was 3.4%.

3.7. Selectivity

The selectivity coefficients for the different anions with respect to perchlorate were calculated for the optode using the activity ratio method [28], in which the selectivity coefficient is measured as the ratio of ion activities or concentrations that generate the same fluorescence when measured in a separate solution type experiment. The calibration graph, Fig. 4(B), was used to calculate the concentration of perchlorate that corresponds to the I_R observed for a certain concentration of interfering ion. The selectivity coefficients were calculated as the ratio of these concentrations:

$$K_{ClO_4^-,X} = C_{ClO_4^-}/C_X$$

Table 2
Determination of anion perchlorate in water

Sample	Content[a]	Found[b]	Recovery %
Tap water	24.9	24.9 ± 0.5	100.0
	49.8	51.7 ± 0.7	103.8
	62.2	63.6 ± 0.2	102.2
Spring water 1	24.9	24.6 ± 0.4	98.9
	49.8	51.1 ± 0.2	102.6
	62.2	62.2 ± 0.4	100.0
Spring water 2	24.9	24.4 ± 0.5	98.0
	49.8	48.5 ± 0.7	97.4
	62.2	60.7 ± 0.4	97.6

[a] μg ml^{-1} ClO_4^- added.
[b] Mean ± standard deviation ($n = 3$).

The resulting selectivity coefficients are shown in Table 1. A very good degree of selectivity with respect to most anions was found.

3.8. Applications

The flow injection method proposed was satisfactorily applied to the determination of perchlorate in water. In the absence of samples containing perchlorate, known amounts of perchlorate were added to different water samples. The result obtained are summarised Table 2. Good recoveries were obtained in all cases.

4. Conclusions

The optode membrane developed for the fluorimetric determination of perchlorate is easily prepared and incorporated in a flow injection system using flow-through cell. The flow-through bulk optode membrane described provides a simple and rapid method for the determination of perchlorate. The sensor was regenerated readily with the same carrier solution and has a long lifetime. The response of the optode was reproducible and the sensor presented good selectivity toward perchlorate. The method permits the determination of perchlorate in water from different sources.

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