

# A double-membrane nitrate ion-selective electrode based on aliquat-nitrate in paraffin

Carmelo Diaz<sup>1</sup>, Juan Carlos Vidal<sup>1</sup>, Javier Galban<sup>1</sup>, M. Angel Navas<sup>1</sup>, and Javier Lanaja<sup>2</sup>

<sup>1</sup> Department of Analytical Chemistry, Faculty of Sciences, University of Zaragoza, E-50009-Zaragoza, Spain

<sup>2</sup> Department of Inorganic Chemistry, University of Zaragoza, E-50009 Zaragoza, Spain

## Nitrationenselektive Doppelmembranelektrode aufgrund von Aliquat-Nitrat in Paraffin

**Summary.** A double-membrane nitrate-selective electrode [as a modified coated wire electrode (CWE)] was prepared with an internal conductor membrane made of tetrabutylammonium bromide (BrTBA) in naphthalene, and an external active membrane (Aliquat-NO<sub>3</sub><sup>-</sup> in paraffin), on an Ag-amalgamated electrode. The nitrate-electrode exhibits linear Nernstian response over the range 1 to 10<sup>-4.5</sup> mol/l of nitrate, with a slope of 56.01 ± 0.9 mV decade<sup>-1</sup>. The selectivity coefficients  $K_{NO_3^-, X}^{Pot}$  for 17 ions were calculated. The effects of pH, membrane composition and thickness were also studied. The life-time of the electrode is 15 days and the stability of its potential is 0.6 mV/12 h. The electrode was preserved dry because of the better sensitivity, range of linear response and detection limit attained. The determination of nitrates in waters and fertilizers was also attempted with this electrode, using the interpolation and standard-addition methods.

## Introduction

Owing to their intrinsic characteristics such as precision, linearity, economy, simplicity, long useful life and speed, the use of ion-selective electrodes (ISEs) for the potentiometric determination of some elements in analytical chemistry has increased considerably, and continues to be an exciting and expanding area of analytical research [2, 7, 8].

One way to reduce the size of conventional ISEs is to remove the internal reference solution, placing the ion-selective material in direct contact with a metal wire [6]. These electrodes, usually PVC based, are called coated wire electrodes (CWEs) [3, 10]. CWEs are easy to build and are versatile, but have low reproducibility and time stability [1].

This paper proposes the addition of an internal conducting membrane to form a double-membrane CWE. The inner membrane gives good reproducibility and time stability, while being faster to make than a conventional polymer membrane.

The inner membrane, whose resistance is 20 kΩ, also gives good electrical conductivity, increased sensitivity, and is fundamental for the electrode response to nitrate ion. The

outer, selective membrane, containing nitrate ion as Aliquat-nitrate solution in 1-decanol dissolved in paraffin [6], is placed over the internal membrane, giving a total electrode resistance of about 1 MΩ.

## Experimental

### Apparatus and reagents

All e.m.f. measurements were made with an Orion Model 901 Microprocessor Ionalyzer pH-millivolt meter. Standard and test solutions were stirred magnetically (30 r.p.m.) with a Teflon bar for 1 min, and the electrode potential response was measured at 25 ± 0.2°C with a precision of ± 0.2 mV.

The membranes were coated on a Beckman Ag cylindrical wire electrode (with a flat surface of about 5 mm diameter). An Orion Model 90-02 double-junction was used as external reference electrode, with aqueous 4 mol/l KCl and 0.02 mol/l (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> as internal and external filling solutions. So the electrochemical cell composition is: Ag / internal membrane / external membrane / sample solution // 0.02 mol/l (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>/3 mol/l LiCl / AgCl-Ag.

All chemicals were of analytical reagent grade. Naphthalene (m.p. 79°–81°C), tetrabutylammonium bromide (BrTBA), tetrahydrofuran (THF), 1-decanol and paraffin (m.p. 51°–53°C) were obtained from Merck. Aliquat 336-S (methyl-tricapryl-ammonium chloride) was obtained from Fluka.

Aliquat-NO<sub>3</sub><sup>-</sup> in 1-decanol solution was prepared by dissolving 12 ml of Aliquat 336-S in 8 ml of 1-decanol and shaking with five 10 ml aliquots of 1.2 mol/l KNO<sub>3</sub> to exchange NO<sub>3</sub><sup>-</sup> for Cl<sup>-</sup>. The aqueous layer was discarded after each extraction, and the organic phase was finally centrifuged to remove traces of water.

An interference suppressor solution (ISS) was prepared by mixing 0.125 g Ag<sub>2</sub>SO<sub>4</sub>, 0.125 g sulphamic acid, 0.125 g Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 0.106 g (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and 0.012 g H<sub>3</sub>BO<sub>3</sub>, and diluting to 25 ml with high purity water in a volumetric flask.

### Electrode Preparation

The Ag electrode was washed with THF, left to dry, and then amalgamated by dipping the base in mercury for 2 min. It was then dipped for 1 s in 3g fused naphthalene (m.p. 79°–81°C) containing 1.2 g BrTBA and 0.5 ml THF (added to reduce the viscosity and control the membrane thickness.

The thickness ( $\delta$ ) of the resulting membrane is about 0.1–0.3 mm.

After being left to dry for 4–5 h, the now solid membrane was coated with the active membrane by dipping for 1 s in 2 g fused paraffin (m.p. 51°–53°C) containing 2 g of Aliquat-NO<sub>3</sub><sup>-</sup>/1-decanol solution and 1 ml THF (to give a thickness of about 0.1 mm). After being left to dry for 12 h, the electrode was conditioned for 1 h in a 0.1 mol/l NH<sub>4</sub>NO<sub>3</sub> solution. The electrochemical system was therefore: Ag / internal membrane / external membrane / sample solution // 0.02 mol/l (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>/3 mol/l LiCl / AgCl-Ag.

## Results and Discussion

### Effect of the composition of the membranes

Initial tests to find the optimum electrode studied PVC (as plasticiser), PhNO<sub>2</sub> (to improve electrode conductivity), Pt electrode and a single membrane, all of which gave inferior analytical results. Amalgamation of the Ag electrode was found to give better electrical contact and membrane adherence (in comparison to Pt), and was adopted. The conducting properties and time response of the electrode appear to depend on the mobility of TBA<sup>+</sup> in the naphthalene matrix.

This conductor membrane is fundamental, in order to obtain the best response of the electrode with nitrate ion. The absence of this membrane gives rise to bad reproducibility and time-stability.

Sensitivity of the electrode also depends on the conductor membrane composition (Fig. 1). In all cases, BrTBA was used to improve the ionic conductivity and THF to reduce the viscosity of solution and make a thinner membrane. Naphthalene was chosen as the inert matrix because of its high m.p. (79°–81°C) in comparison with paraffin (m.p. 51°–53°C). In this study, the active membrane composition was kept constant ( $\delta \approx 0.1$  mm) [Aliquat-NO<sub>3</sub><sup>-</sup> solution/paraffin 1:1 (m/m)].

The sensitivity increases with the concentration of BrTBA in naphthalene. The best results were obtained with a concentration of 40% (m/m) BrTBA/naphthalene (Fig. 1). Concentrations above 40% (m/m) did not change the results.

The principal electrode characteristics (slope, linear response and detection limit) depend on the composition and thickness of the selective external membrane. The best concentration of the electroactive matter (Aliquat-NO<sub>3</sub><sup>-</sup> in paraffin) was determined on the potential response. Figure 2 shows the variation in the calibration graph slope as a function of the active membrane composition. A membrane made with 2 g of Aliquat-NO<sub>3</sub><sup>-</sup> solution in 1-decanol and 2 g of paraffin, exhibits the best results, with a slope of  $56.01 \pm 0.9$  mV decade<sup>-1</sup>. The electrode thus constructed has a response-time less than 40 s for concentrated solutions ([NO<sub>3</sub><sup>-</sup>] = 0.1 mol/l or greater) and about 5 min for dilute solutions (10<sup>-4</sup> mol/l or less).

### Effect of the membrane thickness

It is important to use THF in preparing the internal membrane in order to control the thickness. So, 0.5 ml of THF was added to 4.2 g of BrTBA in melted naphthalene 40% (m/m). Less than 0.5 ml of THF was insufficient to lower the viscosity of the covering solution and more than this

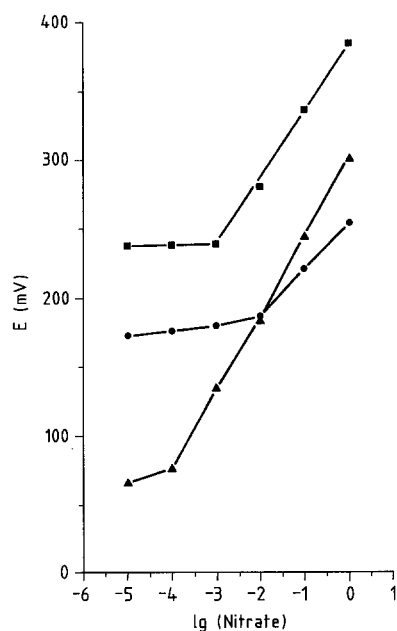


Fig. 1. Effect of the composition of conductor internal membrane on nitrate-selective electrode response (◆ BrTBA / naphthalene 20% (m/m); ● BrTBA / naphthalene 30% (m/m), ▲ BrTBA / naphthalene 40% (m/m). Composition of the outer (active) membrane is paraffin/aliquat-NO<sub>3</sub><sup>-</sup> in 1-decanol 1:1 (m/m)

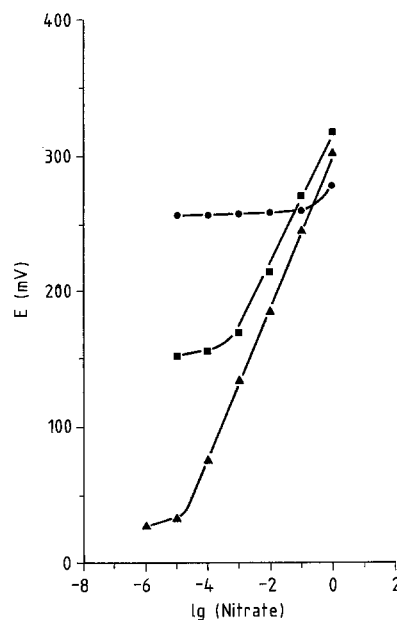


Fig. 2. Effect of the active external membrane composition on nitrate double membrane nitrate-selective electrode response (▲ paraffin / aliquat-NO<sub>3</sub><sup>-</sup> 1:1 (m/m); ◆ paraffin / aliquat-NO<sub>3</sub><sup>-</sup> 0.75:1 (m/m), ● paraffin / aliquat-NO<sub>3</sub><sup>-</sup> 0.50:1 (m/m). Composition of the inner membrane is BrTBA / naphthalene 40% (m/m)

volume was excessive. In the first case, membrane thickness was excessive (lowering sensitivity and increasing the electrode response) and in the second case adherence of the membrane to the amalgamated Ag was bad.

Optimized volume of THF added to the external membrane was 1 ml to 2 g of Aliquat-NO<sub>3</sub><sup>-</sup> solution in 1-decanol and 2 g of melted paraffin.

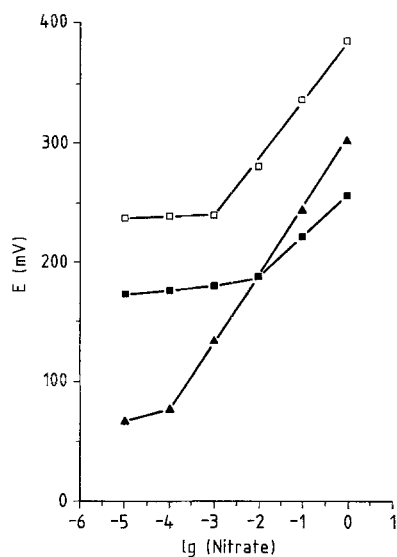


Fig. 3. Effect of electroactive external membrane thickness on the nitrate-selective electrode response ( $\blacktriangle$   $\delta = 0.1$  mm;  $\blacklozenge$   $\delta = 0.3$  mm;  $\diamond$   $\delta = 0.5$  mm). Composition of the inner membrane is BrTBA / naphthalene 40% (m/m)

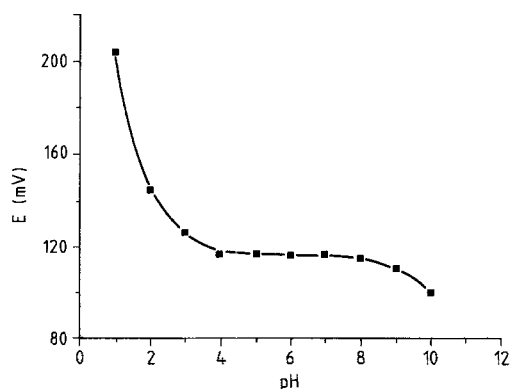


Fig. 4. Effect of pH on the nitrate-selective electrode response

The dipping time of the electrode in the covering solutions is important (1 s for good characteristics of electrode) in the case of both membranes.

If the thickness of the internal membrane is maintained constant, between 0.1–0.3 mm, the electrode response depends on the thickness of the external active membrane (Fig. 3). The best slope, linear range response and response time were obtained with  $\delta = 0.1$  mm. For values above 0.1 mm, the electrode behaviour is subnernstian and linear response is shorter. The electrode response is also slow, with consequent problems of sample contamination.

#### Effect of the pH on the potential response

The effect of the pH on the electrode potential response was studied. 20 ml of a  $10^{-4}$  mol/l  $(\text{NH}_4)\text{NO}_3$  solution, containing 0.4 ml of interference suppressor solution, was prepared. The required pH-value was obtained by addition of dilute HCl (0.1 mol/l) or NaOH (0.5 mol/l) solutions and measured potentiometrically with glass-calomel electrodes.

pH-Values lower than 4 or higher than 8 produce a sharp drop in electrode potential, indicating a potential dependence on pH in this interval (Fig. 4).

#### Electrode performance

Stability of potential of electrode with time was studied ( $[\text{NO}_3^-] = 10^{-3}$  mol/l). A drift of 0.6 mV in 12 h was found, and it is mainly due to draughts or temperature changes.

The response time of electrode ( $t_R$ ) depends on  $\text{NO}_3^-$  activity, ranging from 30 s (for  $[\text{NO}_3^-] \geq 0.1$  mol/l) to about 5 min (for  $[\text{NO}_3^-] \leq 10^{-4}$  mol/l). Influences on electrode response are time and speed of stirring before potential measurement, ionic strength, air bubbles in the membrane of the  $\text{NO}_3^-$  or reference electrodes, etc. Appropriate control of these variables shortens the response time of the electrode.

Stirring the sample solution before potential measurement is also important. From 30 to 150 r.p.m. potential was constant ( $[\text{NO}_3^-] = 10^{-2}$  mol/l) (coefficient of variation for 5 determinations was 1.12%), but speeds above 150 r.p.m. are not advisable owing to splashing. One minute of stirring is sufficient, but the potential must be measured at rest, to avoid drift.

Over the concentration range  $1 - 10^{4.5}$  mol/l of nitrates in final solution, the electrode potential response is linear with the activity of nitrate. The equation of the electrode response is:  $E$  (mV) =  $300.42 - 56.01 \text{ pNO}_3^-$  ( $\pm 1.70\%$  on the basis of measurements with 6 different electrodes) with  $R$ , coefficient of variation, 0.9998 ( $\text{pNO}_3^- = -\log [\text{NO}_3^-]$ ).

The calibration graph slope is  $56.01 \pm 0.9$  mV/ $\text{pNO}_3^-$  and the detection limit calculated as recommended by the IUPAC [5], is  $10^{-5}$  mol/l  $\text{NO}_3^-$ .

The reproducibility (ten replicate determinations) in the determination of  $10^{-4}$  mol/l nitrate, was established. The standard deviation was 2.44 ( $\bar{x}$ , mean of potential, 22.2 mV) and relative standard deviation was 1.10%. Reproducibility results are similar to the values of commercial  $\text{NO}_3^-$  ion-selective electrodes—typical values ranged from 0.5% (e.g. Radiometer F 2412 or Philips 561) to 2.0% (e.g. Orion 93-07 or Ingold 152223000).

#### Conditioning of electrode

The electrode was kept in high purity water, nitrate solution 0.1 mol/l or dry, observing changes in its analytical characteristics (linearity, sensitivity and detection limit). Results indicate that the electrode has to be kept dry if not in use. Otherwise it deteriorates and its performance is impaired. Kept dry, electrode life time was about 15 days.

Nevertheless, conditioning of electrode before use for 1 h in a solution 0.01–0.1 mol/l of nitrate is essential. Otherwise, response time is long and reproducibility poor.

Memory effects due to contamination (adsorption) of external membrane with successive solutions are easily eliminated by cleaning the base of electrode with high purity water before use and magnetically stirring (30 r.p.m.) test solution for 1 min prior to potential measurements. In the case of clinical samples, with a high content of proteins, adsorption can be avoided with addition to trypsin or triethanolamine [11].

To get correct response, it is not necessary to submerge the base of electrode completely into the sample solution, but only to touch the tip of the base with this solution submerging only the membranes or the area containing

them. This aspect is of interest when small volumes of test solutions are available (e.g. biochemical or clinical samples).

### Interference study

Selectivity coefficients ( $K_{NO_3^-, X}^{Pot}$ ) of the nitrate-selective electrode were calculated by the mixed solution method [13, 14], from potential measurements on 20 ml of a solution containing a fixed nitrate concentration ( $10^{-4}$  mol/l of nitrate) (plus 0.4 ml of ISS) and varying the interferent ion concentration by adding small volumes ( $V$ ) of an interferent ion solution (1 mol/l). Assuming that the electrode membrane is not seriously affected by the presence of the interferent ion, in the case of  $Z_A = Z_B$  ( $Z_A$  and  $Z_B$  are the charge numbers of ions A and B respectively) [9]:

$$[A] = (C_A V^0)/(V^0 + V) \quad (\text{concentration of nitrate})$$

$$[B] = (C_B V)/(V^0 + V) \quad (\text{concentration of interferent})$$

with:

$$C_A = \text{nitrate ion initial concentration} = 9.8 \cdot 10^{-5} \text{ mol/l.}$$

$$V^0 = \text{nitrate solution initial volume} = 20.04 \text{ ml.}$$

$$C_B = \text{interferent ion initial concentration} = 1 \text{ mol/l and}$$

$$V = \text{volume of interferent solution added (0.5, 1.0, 1.5 and 2.0 ml).}$$

Introducing these concentrations into the Eisenman-Nicolosky equation:

$$(V^0 + V) 10^{E/S} = 10^{E^0/S} [C_A V^0 + K_{A,B} (C_B V)^{Z_A/Z_B} (V^0 + V)^{Z_B - Z_A/Z_B}]$$

If  $Z_A = Z_B$ , a straight-line is obtained, and the coefficient of selectivity ( $K_{NO_3^-, X}^{Pot}$ ) can be calculated experimentally by extrapolation for  $\emptyset = 0$  of  $V$  (obtaining  $V_X$ ), where  $\emptyset$  is the function:

$$\emptyset = (V^0 + V) 10^{E/S}$$

with:

$$V = \text{volume of interferent added.}$$

$$E = \text{electrode potential.}$$

$$S = \text{slope of the calibration graph.}$$

Then:

$$K_{NO_3^-, X}^{Pot} = -(C_A V^0)/(C_B V_X) \quad (1)$$

If  $Z_A < Z_B$ , and if maximum added volume is negligible with respect to  $V^0$  (initial),  $V_X$  can be calculated by extrapolation of  $\emptyset$  against  $V^{Z_A/Z_B}$ , then equation:

$$K_{NO_3^-, X}^{Pot} = -C_A (V^0/C_B V_X)^{Z_A/Z_B} \quad (2)$$

was used.

For  $C_A = 10^{-4}$  mol/l and  $C_B = 1$  mol/l the calculated coefficients of selectivity appear in Table 1.

After studying each interfering ion, electrodes were washed with abundant high purity water, and carefully dried with a fine filter paper.

$SCN^-$ ,  $ClO_3^-$  and  $ClO_4^-$  appear to be the principal interfering anions. Chlorate and perchlorate anions proved to attack the constructed electrode, and after using the electrode in solution with these anions, construction of new membranes for nitrate ion-selective electrode is advisable.

### Applications

The proposed electrode was applied to determine nitrate in natural waters and fertilizers by interpolation on the

**Table 1.** Selectivity coefficients ( $K_{NO_3^-, X}^{Pot}$ ) of various ions with the nitrate-electrode based on Aliquat- $NO_3^-$ /paraffin

Ion (X)	( $K_{NO_3^-, X}^{Pot}$ )	Ion (X)	( $K_{NO_3^-, X}^{Pot}$ )
$F^-$	$6.81 \cdot 10^{-4}$	$CO_3^{2-}$	$-1.28 \cdot 10^{-4}$
$Cl^-$	$3.20 \cdot 10^{-3}$	$HCO_3^-$	$0.69 \cdot 10^{-4}$
$Br^-$	$1.28 \cdot 10^{-3}$	$NO_2^-$	$1.27 \cdot 10^{-2}$
$I^-$	$3.76 \cdot 10^{-3}$	$H_2PO_4^-$	$-3.65 \cdot 10^{-5}$
$CN^-$	$2.13 \cdot 10^{-2}$	$HPO_4^{2-}$	$1.98 \cdot 10^{-3}$
$SCN^-$	-13.15	$PO_4^{3-}$	$-1.84 \cdot 10^{-4}$
$SO_4^{2-}$	$7.75 \cdot 10^{-4}$	$ClO_3^-$	$-3.74 \cdot 10^{-2}$
$S^{2-}$	$3.86 \cdot 10^{-4}$	$ClO_4^-$	$-1.33 \cdot 10^{-2}$
Acetate	$-2.28 \cdot 10^{-4}$		

**Table 2.** Results of the determination of nitrate in waters and fertilizers (Mean value and coefficient of variation)

Sample	Method 1	Method 2	Method 3
1	1.5 (1.05%)	1.6 (1.12%)	1.6 (2.20%)
2	0.9 (1.02%)	0.90 (1.17%)	0.80 (2.26%)
3	12.4 (1.10%)	13.1 (1.22%)	12.6 (2.56%)
4	22.5 (1.14%)	22.7 (1.54%)	23.0 (2.44%)
5	78.2 (1.88%)	79.0 (1.43%)	78.6 (2.64%)
6	88.3 (1.74%)	88.5 (2.01%)	90.3 (2.58%)

*Samples:* 1 Huerva river water (Zaragoza, Spain) (Jan 10, 1987). Values in  $\mu\text{g ml}^{-1}$ ; 2 Ebro river water (Zaragoza, Spain) (Jan 18, 1987). Value in  $\mu\text{g ml}^{-1}$ ; 3 Irrigation water (Zaragoza, Spain) (Jan 26, 1987). Values in  $\mu\text{g ml}^{-1}$ ; 4 Industrial waste water (Zaragoza, Spain) (Feb. 9, 1987). Values in  $\mu\text{g ml}^{-1}$ ; 5 ERT Fertilizer 1 (33.5% N). Values in %  $NO_3^-$ ; 6 ERT Fertilizer 2 (38.5% N). Values in %  $NO_3^-$ . *Method 1* Interpolation on the calibration graph ( $n = 6$ ); *Method 2* Double addition ( $n = 4$ ); *Method 3* Spectrophotometric ( $n = 4$ )

calibration graph and standard-addition methods. The results obtained were compared with those obtained by the Brucine spectrophotometric method [12], used as standard method. The concentrations obtained by the nitrate-selective electrode showed good agreement with those obtained spectrophotometrically (Table 2).

Procedure for nitrate determination was as follows: place 20 ml of test solution in a double-walled vessel (thermostated at  $25^\circ \pm 0.2^\circ\text{C}$ ). Add 0.4 ml of interference suppressor solution (ISS) and 5 ml acetate/0.1 mol/l acetic acid pH 4.50 buffer solution. Stir the solution magnetically (30 r.p.m.) for 1 min. Place both electrodes, nitrate selective and double junction reference, in the vessel, and allow the electrochemical cell to reach potential stability ( $\pm 0.2$  mV).

Addition of interference suppressor solution (ISS) is used for:  $(NH_4)_2SO_4$  to adjust the solution ionic strength,  $Ag_2SO_4$  to precipitate halides,  $CN^-$ ,  $SCN^-$  and  $S^{2-}$ , sulfamic acid to reduce nitrite (not nitrate),  $Al_2(SO_4)_3$  to complex organic anions and  $H_3BO_3$  to eliminate biological degradation of samples. Acetate buffer (pH 4.50) eliminated  $HCO_3^-$  and  $CO_3^{2-}$  from samples as  $CO_2$ .

Adjustment of ionic strength of samples is critical due to its influence on selectivity coefficients and the liquid-junction potentials of electrochemical cell. So, addition of ammonium sulphate is very important in order to adjust I (ionic strength) from 0.1 to 2 mol/l.

### Conclusion

It can be concluded that the constructed nitrate-selective electrode, based on an internal conductor membrane of BrTBA in naphthalene and external active membrane of aliquat-NO<sub>3</sub><sup>-</sup> in paraffin, exhibits good sensitivity with a nernstian slope ( $56.01 \pm 0.9$  mV decade<sup>-1</sup>), a good detection limit ( $10^{-5}$  mol/l), good reproducibility (1.05% relative standard deviation) and selectivity. The construction procedure is inexpensive and easy. The electrode has successfully been applied to the determination of nitrate in natural waters and fertilizers.

### References

1. Arnold MA, Meyerhoff ME (1984) *Anal Chem* 56:20R–48R
2. Arnold MA, Solsky RL (1986) *Anal Chem* 58:84R–101R
3. Cattrall RW, Hamilton IC (1984) *Ion-Sel Electrode Rev* 6:125
4. Freiser H, Cattral RW (1971) *Anal Chem* 43:1905
5. IUPAC (1976) *Pure Appl Chem* 48:27
6. Kneebone BN, Freiser H (1973) *Anal Chem* 45:449
7. Korita J (1984) *Anal Chim Acta* 159:1
8. Korita J, Stulik K (1983) In: *Ion-selective electrodes*, 2nd edn. Cambridge University Press, Cambridge
9. Macca C, Cakrt M (1983) *Anal Chim Acta* 51:154
10. Moody GJ, Thomas JDR (1984) *Ion-Sel Electrode Rev* 6:109
11. ORION Newsletter (1971) III:35
12. *Official Methods of Analysis of the Association of Official Analytical Chemists* (1975) Ed AOAC (USA), p 614
13. Pungor E, Toth K, Hrabczy P (1979) *Pure Appl Chem* 51:1913
14. Srinivasan K, Rechnitz GA (1969) *Anal Chem* 41:1203

Received July 18, 1988; revised November 26, 1988