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ION CHROMATOGRAPHIC DETERMINATION OF NITRITE IN THE PRESENCE OF A LARGE AMOUNT OF CHLORIDE

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SUMMARY

Different procedures for the quantitation of nitrite in the presence of a large excess of chloride are described. The results obtained show that, in general, solutions characterized by NO_2^-/Cl^- ratios of about 1/10 000 can very easily be analyzed. The best results were obtained with amperometric detection in conjunction with NaCl as the eluent which allows ratios down to about 1/700 000 to be employed. One of the procedures investigated was successfully applied to the analysis of samples of sea-water from fish breeding pools.

INTRODUCTION

The use of different detectors, *i.e.*, conductometric, spectrophotometric and amperometric, has widened the application of ion chromatography (IC) to the determination of inorganic ions in a variety of aqueous matrices[1]. Nitrite ion, in particular, can be determined by the universal conductometric procedure[2], by oxidation at a glassy carbon electrode[3] and by UV absorbance detection[4]. The determination of nitrite ion is indeed of particular importance since it is largely used in the food industry and because it is able to reveal, in environmental analyses, organic contaminations[5]. Samples, on the other hand, often have an high content of other interfering ions so that the direct use of IC can be severely limited. The presence of a large amount of chloride is a typical drawback in the determination of traces of nitrite since the tail of the chloride peak can obscure the nitrite peak. The present paper reports on the problem of determining, following different approaches, traces of nitrite at very low nitrite to chloride concentration ratios. In particular, the potential of different procedures employing always the same general purpose column was tested

and compared: a mixed H_3BO_3–Na_2CO_3 eluent with an anion membrane suppressor followed by a conductivity detector, UV and glassy carbon amperometric detectors in conjunction with different eluents. Moreover, an application to real sea-water samples drawn from fish-breeding pools was performed.

EXPERIMENTAL

Chemicals and reagents

Unless otherwise stated, all chemicals were of analytical reagent grade. Demineralized water was passed through a Millipore cartridge (GS 0.22 μm) for final purification and deaerated. Nitrite standards (1000 ppm and lower concentrations) were prepared according to the literature[6]. The following set of solutions were used as eluents in the chromatographic tests: 1.8 mM Na_2CO_3–1.7 mM $NaHCO_3$; 0.5 mM Na_2CO_3–2 mM H_3BO_3; 20 mM NaCl; 25 mM H_2SO_4 for regenerating the anion membrane suppressor. For the preparation of the sodium chloride eluent, an high quality reagent, 99.999% Aldrich NaCl, was used to avoid problems due to traces of more strongly retained anions, I^-, etc.

Apparatus and procedure

A Dionex Model 2010i ion chromatograph was used throughout this study. Chromatograms were recorded either on an AMEL x–y recorder or on a Spectra-Physics Model 4290 integrator. The column, obtained from Dionex, was a general purpose 250 mm × 4.0 mm AS4A column in conjunction with a 50 mm × 4.0 mm AG4A guard column. A 50-μl sample loop was used for all injections. A Dionex conductivity detector, a variable wavelength Model 8987 UV–VIS Knauer detector and an EG&G PAR Model 400 detector were employed. Preliminary UV spectra were recorded by using a Perkin-Elmer Model Lamda 5 spectrophotometer and an EG&G PAR Model 273 potentiostat was used in the unitial electroanalytical investigations. The pH of the eluent solutions was measured with a Metrohm Model 654 pH meter. In order to obtain the data for deconvolution of the overlapped peaks of Cl^- and of NO_2^-, the experimental curves obtained with the H_3BO_3 eluent were digitalized by a graphic digitalizer, Houston instruments "True Grid" Model 1017. The two contributors to the detector response were described by a suitable mathematical model. A gaussian function

$$y = a_1 \exp\left[-\frac{1}{2}[(x - a_2)/a_3]^2\right] \tag{1}$$

(where x is the time and y the response of the conductometric detector) was used to represent the nitrite peak, while an hyperbola

$$y = a_4 \cdot \frac{1}{x - a_5} + a_6 \tag{2}$$

was fitted to the chloride tail. The parameters of the mathematical model

$$y(x, \bar{a}) = a_1 \exp\left[-\frac{1}{2}[(x - a_2)/a_3]^2\right] + a_4 \cdot \frac{1}{x - a_5} + a_6 \tag{3}$$

were obtained by means of a non-linear regression routine, the Simplex procedure[7], which minimized the sum of the squares of the differences between the experimental and computed data points. The programs used, written in FORTRAN IV, were run under a RT-11 operating system on a PDP 11/23 Digital computer equipped with a Tektronix Model 4662 plotter.

RESULTS AND DISCUSSION

Preliminary considerations

The determination, by ion chromatography, of traces of nitrite in the presence of a large amount of chloride is usually accomplished by eliminating, on a silver-loaded cation-exchange resin, the excess of chloride ions[8]. This procedure, however, can be quite tedious, expensive and potentially harmful to the chromatographic column since traces of heavy metals are strong poisons of it. Even when addition of NaI to the analyte solution eliminated the above mentioned danger, owing to the very low value of the solubility product of AgI, attempts were made to overcome all the drawbacks either by finding a new eluent able to produce a better separation between chloride and nitrite, or by employing different detection procedures.

H_3BO_3–Na_2CO_3 eluent and conductivity detection

Literature data[1] indicate that different pH values of the eluent, that is different ratios between $NaHCO_3$ and Na_2CO_3, do not affect appreciably the ratio of the capacity factors, k', for nitrite and chloride ions. Therefore the strong tailing of the chloride peak always prevents the detection of a small nitrite peak. The presence of H_3BO_3 in the eluent implies, on the other hand, two different effects, namely a slight

TABLE I

CAPACITY FACTORS AND PEAK WIDTHS (4σ) OF NO_2^- FOR DIFFERENT Na_2CO_3–H_3BO_3 CONCENTRATIONS IN THE PRESENCE OF A LARGE AMOUNT OF Cl^- (500 ppm)

Chromatographic conditions: sample volume, 50 μl; flow-rate, 2 ml min^{-1}; detector, suppressed conductivity.

Eluent (M)		Capacity factor, k'	Peak width (s)
Na_2CO_3	H_3BO_3		
$2.5 \cdot 10^{-4}$	$2 \cdot 10^{-3}$	29.11	72.5
$5 \cdot 10^{-4}$	$2 \cdot 10^{-3}$	14.11	34
$1 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	7.44	17.5
$2 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	—[a]	—[a]
$5 \cdot 10^{-4}$	$1 \cdot 10^{-3}$	11.44	20
$5 \cdot 10^{-4}$	$2 \cdot 10^{-3}$	14.11	34
$5 \cdot 10^{-4}$	$3 \cdot 10^{-3}$	17.22	44
$5 \cdot 10^{-4}$	$4 \cdot 10^{-3}$	19.88	52.5
$2.5 \cdot 10^{-4}$	$1 \cdot 10^{-3}$	22.11	44
$5 \cdot 10^{-4}$	$2 \cdot 10^{-3}$	14.11	34
$1 \cdot 10^{-3}$	$4 \cdot 10^{-3}$	10.22	27.5

[a] No separation.

increment in the difference between the k' values and mainly a strong effect in reducing the tail of the chloride peak. On the basis of these findings, H_3BO_3 was added to the eluent, to improve the separation by modifying the shape of the larger peak. Several tests, performed with different concentrations of H_3BO_3 and Na_2CO_3 (see Table I), indicated that a suitable composition of the eluent was 2 mM H_3BO_3 and 0.5 mM Na_2CO_3 which results in a pH of 8.4. Fig. 1 shows, via a logarithmic diagram, that the main species present in the eluent solution are H_3BO_3 and HCO_3^-. Therefore the active ionic species in the eluent is HCO_3^-, while H_3BO_3 plays the rôle of a fronting agent. Since the analytical column works best with a low ionic loading of the sample solution, high chloride to nitrite ratios can be analyzed only by reducing, by proper dilution, the overall concentration and taking advantage of the high sensitivity of the detector. A chromatogram of a sample containing only 0.1 p.p.m. of NO_2^- is still well developed (see Fig. 2a) with a coefficient of variation of about 3%. By adding 500 ppm of Cl^- to 0.1 ppm of NO_2^- a complete resolution was not achieved (Fig. 2b), but deconvolution of the data as described above gave the response shown in Fig. 2d. The correctness of the mathematical model (eqn. 3) is demonstrated by the fitted curve shown in Fig. 2c, which is quite close to that in Fig. 2b. It is evident that the deconvolution method adopted allows the area of the nitrite peak to be evaluated by means of the eqn. 1. Therefore, the limiting Cl^- to NO_2^- ratio for this procedure is about 500/0.05, which results in a precision quite close to that of the analysis of NO_2^- alone.

Of interest is that the retention times for NO_2^- alone and in presence of a large amount of Cl^- do not coincide. This difference, about 1 min, can be explained by taking into account the weaker eluent strength of Cl^- in comparison with HCO_3^-. With a large chloride loading, it can be assumed that HCO_3^- is substituted as the eluent ion by Cl^- in the neighbourhood of the NO_2^- band. Fig. 3 compares the responses at six different nitrite concentrations, in the range 0.1–1 ppm, obtained in absence and in
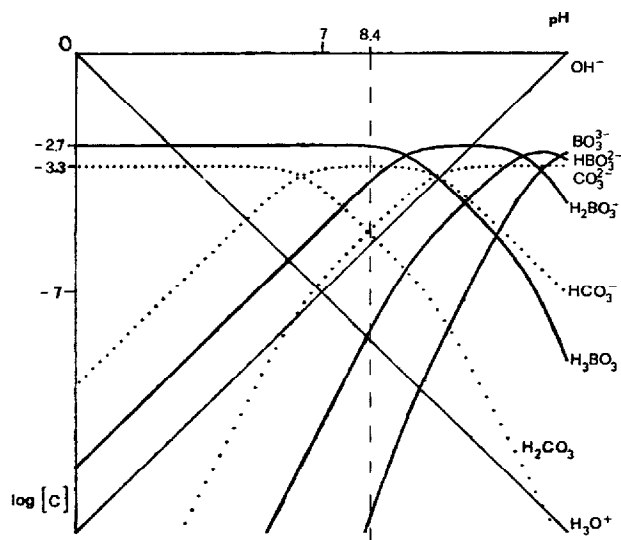

Fig. 1. Logarithmic diagram (pH *vs.* log[C]) for the Na_2CO_3–H_3BO_3 eluent. Eluent composition: 2 mM H_3BO_3 and 0.5 mM Na_2CO_3.
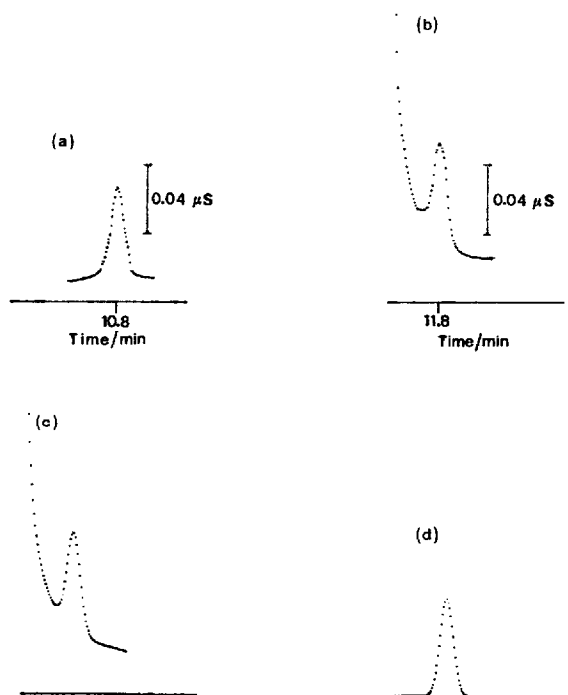
Fig. 2. (a) Digitalized ion chromatographic response of a 0.1 ppm aqueous solution of NO_2^-. (b) Digitalized ion chromatographic response of a 0.1 ppm aqueous solution of NO_2^- in the presence of 500 ppm Cl^-. (c) Fitted chromatogram of an aqueous solution containing 0.1 ppm NO_2^- and 500 ppm Cl^-. The model used was a Gaussian function plus an hyperbola. The parameters were estimated by a Simplex algorithm. (d) Peak of NO_2^- after deconvolution of the two components as described in (c). Chromatographic conditions: sample volume, 50 μl; flow-rate, 2 ml min^{-1}; detector, suppressed conductivity; mobile phase, 2 mM H_3BO_3 and 0.5 mM Na_2CO_3 in water.

the presence of chloride after the data handling. The fact that the points lie on a straight line of unit slope indicates that the chloride excess does not influence the nitrite peak. Two disadvantages, however, have to be mentioned. Some ions, SO_4^{2-} or PO_4^{3-} for instance, are retained too strongly with the $H_3BO_3–Na_2CO_3$ eluent and the performance of the analysis is obviously strongly dependent on the behaviour of the column. An aged column, yielding markedly shortened retention times, prevents a satisfactory resolution of the peaks.

NaHCO₃–Na₂CO₃ eluent and spectrophotometric detection

Using the classical $NaHCO_3$ Na_2CO_3 eluent, the selectivity of the spectro-photometric detector allows the determination at 210 nm of traces of nitrite in the presence of a large amount of chloride, since chloride absorbs weakly in the UV region only below 200 nm. As reported in the literature[4] and also demonstrated by us, the suppressor membrane, besides decreasing the high background electrical conductance of the eluent, also decreases the high background absorbance of the eluent in the range 190–220 nm because the extinction coefficient of a solution of H_2CO_3 is lower than
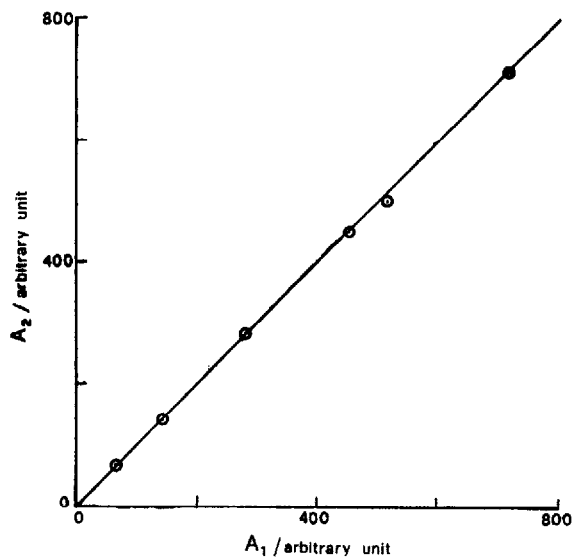
Fig. 3. Plot of the peak areas of NO_2^-, A_2, *vs.* the peak areas of NO_2^- in the presence of 500 ppm Cl^-, A_1. Concentration range of NO_2^- : 0.1–1.0 ppm. The areas were computed after the fitting procedure described in Fig. 2c. Regression plot: $A_2 = a + bA_1; a = 1.39 \pm 4.67; b = 0.99 \pm 0.1; \rho = 0.9998$. Chromatographic conditions as in Fig. 2.

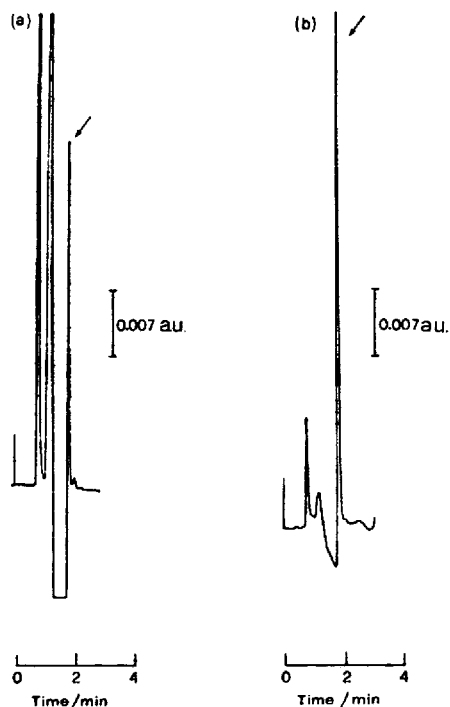Fig. 4. Ion chromatographic responses of 1 ppm. NO_2^- and of 500 ppm Cl^- without (a) and with (b) the suppressor membrane and UV detection. Chromatographic conditions: sample volume, 50 μl; flow-rate, 2 ml min^{-1}; wavelength, 210 nm; mobile phase, 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ in water.

that of one of $HCO_3^- \text{-} CO_3^{2-}$. Therefore, the configuration with the UV detector inserted after the membrane suppressor was adopted for higher sensitivity and higher reproducibility. Fig. 4a and b shows two chromatograms obtained without and with the suppressor. It is seen that the broad negative peak due to the chloride ion eluted before NO_2^- is strongly reduced, as expected on the basis of the above arguments, upon insertion of the membrane suppressor. Since NO_2^- is only one of the pollutants potentially present in sea-water, the experimental device described was also tested to determine whether it were possible to measure other contaminants, like NO_3^- and PO_4^{3-}, in the same chromatographic analysis, which is a strong requirement advanced by environmental analysts[9]. The approach described gives quite good results for NO_3^- but, of course, does not allow the determination of PO_4^{3-} as a consequence of its lack of absorption. This ion, however, does not suffer any interference from the presence of chloride because of its long retention time, so that the use of the conductometric detector, connected in series with the UV detector, is suggested for the determination of PO_4^{3-} (ref. 10). Fig. 5a and b shows the chromatographic responses relative to a mixture of 0.25 ppm of NO_2^-, NO_3^- and PO_4^{3-} in the presence of 1000 ppm of Cl^- obtained with UV (Fig. 5a) and conductometric (Fig. 5b) detectors. The eluent in this case was 0.002 M Na_2CO_3 aqueous solution. It was chosen because of the requirement of using the lowest concentration of H_2CO_3 which gave the smallest dip while
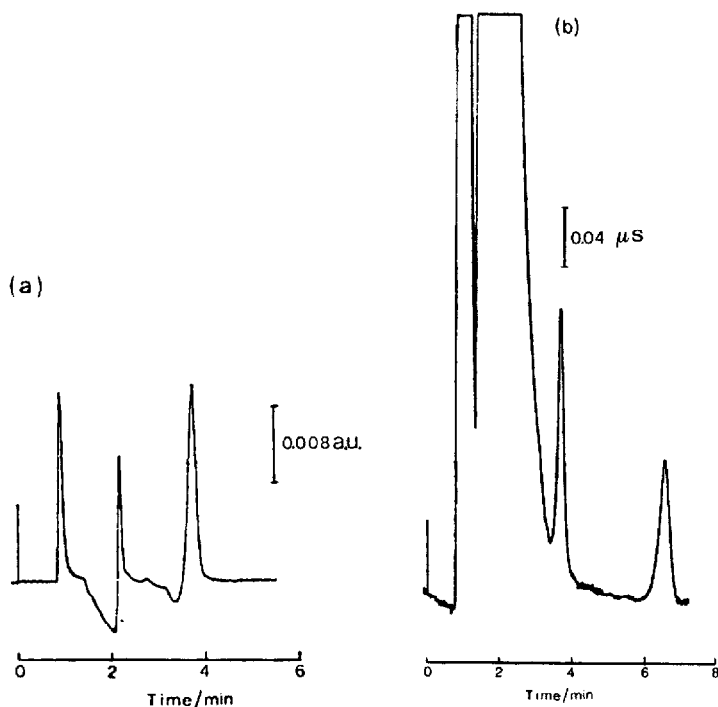

Fig. 5. Ion chromatographic response of 0.25 ppm of NO_2^-, 0.25 ppm NO_3^- and 0.25 ppm PO_4^{3-} in the presence of 1000 ppm of Cl^- obtained with UV (a) and conductometric detection (b). Chromatographic conditions: sample volume, 50 μl; flow-rate, 2 ml min^{-1}; wavelength, 210 nm (a); mobile phase, 0.002 M Na_2CO_3 in water.
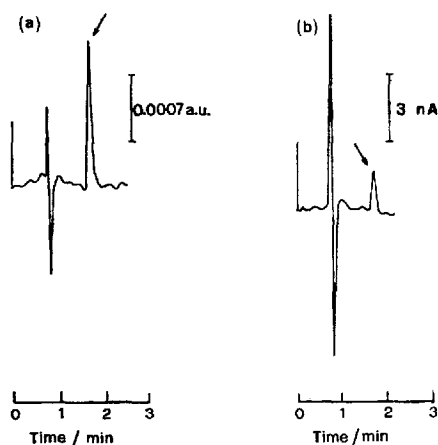
Fig. 6. (a) Ion chromatographic response of 0.03 ppm NO_2^- in the presence of 500 ppm. Cl^- obtained by UV detection. Chromatographic conditions: sample volume, 50 μl; flow-rate, 2 ml min^{-1}; wavelength, 210 nm; mobile phase, 0.02 M NaCl in water. (b) Ion chromatographic response of 0.007 ppm NO_2^- in the presence of 500 ppm Cl^- obtained by amperometric detection. Chromatographic conditions: sample volume, 50 μl; flow-rate, 2 ml min^{-1}; $E = 1$ V; mobile phase, 0.01 M NaCl in water; working electrode, glassy carbon; counter electrode, Pt; reference electrode Ag/AgCl saturated KCl.

maintaining a good eluent strength. According to the procedure reported in ref. 11, the detection limit for NO_2^- (as 3σ of the baseline noise) was 0.01 ppm so that the limiting ratio for NO_2^-/Cl^- is 1/50 000.

NaCl eluent and spectrophotometric and amperometric detection

Since the excess of chloride in the sample solution can cause instability of the analytical column (broad positive and negative preceding peaks), the use of the chloride ion itself as the eluent was taken into account. With this new eluent the baseline has to be best possible and with an appropriate concentration (0.02 M) the retention time of NO_2^- is practically equal to that obtained with $HCO_3^- - CO_3^{2-}$ as the eluent. Fig. 6a shows a chromatogram of 500 ppm of Cl^- and 0.03 ppm of NO_2^-. However, caution must be exercised in using this eluent. The usual analytical reagent grade NaCl contains traces of I^- and other ions which are more strongly retained on the column. For this reason, after several hours of elution, they are removed from the column causing an undesired flicker noise in the baseline and ghost peaks with both detectors. When no instability occurs, the limiting ratio obtainable by this procedure is determined only by the detection limit relative to NO_2^-. Since the detection limit of NO_2^- is[11] about 0.005 ppm with a spectrophotometric detector at 210 nm, the limiting ratio Cl^-/NO_2^- can decrease to 1000/0.005, *i.e.*, 200 000/1. With the amperometric detector, working at an appropriate oxidation potential (*ca.* 900 mV *vs.* Ag/AgCl saturated KCl), not only the selectivity with respect to NO_2^- is maintained but also an advantage is obtained from the ability of chloride ion to enhance the electrochemical reversibility of many oxidation processes[12]. Fig. 6b shows a chromatogram of 500 ppm of Cl^- and 0.007 ppm of NO_2^-. On the basis of the above considerations, it can be stated that a detection limit of about 0.0014 ppm is easily achieved and consequently
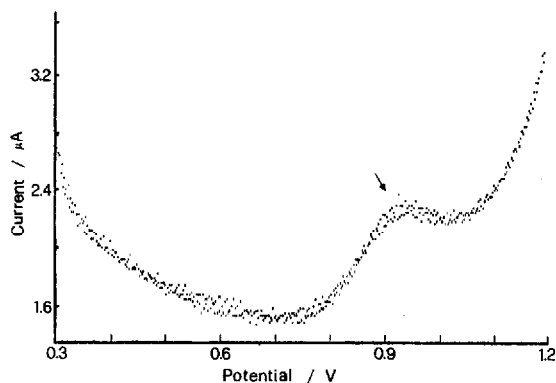
Fig. 7. Square wave voltammetric response of 0.9 ppm NO_2^- in 2500 ppm Cl^- in aqueous solution. Conditions: step height, 2 mV; pulse amplitude, 50 mV; frequency, 20 Hz. Electrodes as in Fig. 6b. The arrow indicates NO_2^-.
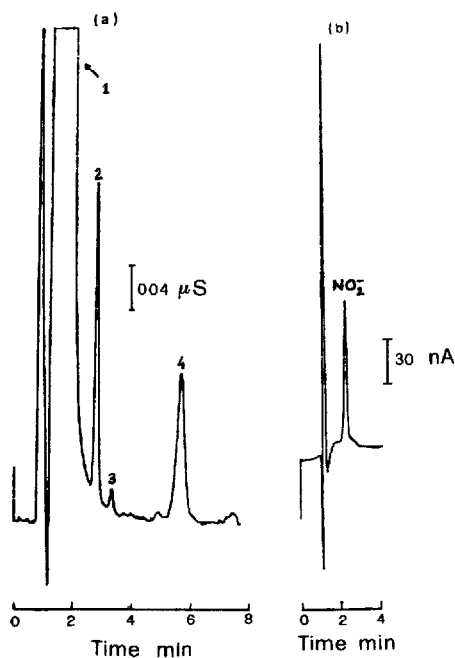

Fig. 8. (a) Ion chromatographic response obtained with conductometric detection for a real sample of sea-water diluted 20-fold. Peaks: 1 = Cl^- and NO_2^-; 2 = Br^-; 3 = NO_3^-; 4 = PO_4^{3-}. Chromatographic conditions: sample volume, 50 μl; flow-rate, 2 ml min^{-1}; detector, suppressed conductivity; mobile phase, 0.002 M Na_2CO_3 in water. (b) Ion chromatographic response obtained with amperometric detection of the same sample. Chromatographic conditions: sample volume, 50 μl; flow-rate, 2 ml min^{-1}; $E = 1$ V; mobile phase, 0.02 M NaCl in water; working electrode, glassy carbon; counter electrode, Pt; reference electrode, Ag/AgCl/saturated KCl.

the limiting ratio is about 715 000/1. In this connection it can be noted that a sensitive electroanalytical technique, namely square wave voltammetry, gives a detection limit for NO_2^- of only about 0.9 ppm as shown in Fig. 7. This is in accord with the general statement that, on passing from an unstirred solution to a flowing solution, using an appropriate thin-layer detector, a relevant enhancement in sensitivity is generally obtained[13]. One drawback has been pointed out for the suggested analytical system. After some hours of elution, a quite slow passivation of the electrode surface causes an increasing loss of sensitivity of the detector. For this reason the internal standard method is more suitable than the use of a calibration graph. However, the usual polishing with Al_2O_3 restores the optimum performance of the detector.

Analysis of real samples

The quality control of water in fish breeding plants is of obvious importance and NO_2^- is one of the most important species whose concentration has to be monitored. For this kind of analysis the approaches described above have been utilized. Since the real samples contained about 20 000 ppm of Cl^- (sea-water) and very low concentrations of NO_2^- we used the amperometric detector. This procedure was quite satisfactory as demonstrated by Fig. 8 which compares the responses of a real sample diluted 1 to 20 recorded with the conductometric (Fig. 8a) and the amperometric (Fig. 8b) detectors. In the first case the tail of the chloride peak overlaps the bromide one, while the amperometric detector exhibits an excellent response which gives a value of 0.35 ppm NO_2^- with a coefficient of variation of less than 0.5%.

CONCLUSIONS

The results in Table II clearly indicate that the analytical procedures examined are suitable for the quantitation of NO_2^- in the presence of a large excess of chloride ion, even when using a general purpose analytical column. Concentrations of NO_2^- higher than those reported are, of course, easier to determine owing to the general linear response of NO_2^- (up to 10 ppm) even in the presence of the large excess of Cl^-. Dedicated experimental devices, *i.e.*, spectrophotometric and amperometric detectors with NaCl as the eluent, give the best performance, allowing the determination of NO_2^- in sea-water at very low concentrations, but quite satisfactory results can be still obtained when only the eluent composition is changed and the general purpose conductivity detector is employed.

TABLE II

DETECTION LIMITS (DL) IN THE PRESENCE OF CHLORIDE AND LIMITING RATIOS FOR THE DIFFERENT ELUENT–DETECTOR COMBINATIONS INVESTIGATED

Eluent	Conductometric		UV		ED	
	DL NO_2^- (ppm)	Cl^-/NO_2^-	DL NO_2^- (ppm)	Cl^-/NO_2^-	DL NO_2^- (ppm)	Cl^-/NO_2^-
$HCO_3^- - CO_3^{2-}$	0.1	200	0.01	50 000	—	—
$H_3BO_3 - CO_3^{2-}$	0.05	10 000	—	—	—	—
NaCl	—	—	0.005	200 000	0.0014	715 000

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