



ELSEVIER

Journal of Chromatography A, 706 (1995) 277–280

JOURNAL OF
CHROMATOGRAPHY A

Ion chromatographic determination of nutrients in sea water

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Abstract

The application of ion chromatography, with eluent suppression and conductometric detection, to the determination of nitrate and phosphate concentrations in sea water was investigated. The aim was to evaluate the concentration of both species simultaneously and without the need to pretreat the sample, thus avoiding the disadvantages inherent in the usual analytical methods (molecular spectroscopy of suitable derivatives). The determination of nitrate was also accomplished using UV detection at 210 nm by means of a diode-array detector connected in series with the conductivity detector. In this way, by comparing the absorption spectra of nitrate in the standard solution and in the samples and by checking the purity index of the related peaks, the effectiveness of the chromatographic separation and the lack of interferences in the analysis were monitored. About 40 samples of sea water, taken over several months in four different locations, were analysed after filtration and dilution. In all the samples nitrate was detectable and the separation between the peaks of nitrate and bromide was complete, even when the bromide concentration was as high as 70 ppm. Only some of the samples, owing also to the nearly always necessity for dilution, showed a concentration of phosphate higher than the limit of detection.

1. Introduction

Some areas of the Italian coastline are affected by eutrophication. In such cases, Italian legislation requires that the regions activate plans for biological and chemical control. As nitrate and orthophosphate are among the chemical species to be evaluated, we directed our efforts towards the achievement of an analytical method that could be both reliable and rapid.

2. Experimental

2.1. Samples

Samples of sea water were taken in four

resorts on the Tyrrhenian coast, Calambrone, Naval Academy, Tre Ponti and Chioma. Chioma lies about 7 km to the south of the town of Leghorn (Tuscany), while Calambrone lies about 4 km to the north of the town and about 9.5 km to the south of the mouth of the river Arno. Naval Academy and Tre Ponti are situated on the town coastline. The samples were taken in the period from January 1992 until May 1993, at a distance of about 0.5 m from land and at a depth of about 40 cm. They were put in polyethylene bottles and kept at 4°C until analysis. Aliquots of 5 ml were usually diluted five- or tenfold with analytical-reagent grade water (specific resistance >18 MΩ cm); they were then filtered through 0.45-μm filters and finally injected.

The samples taken at Calambrone always showed a lower salinity, owing to the proximity

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of the mouth the river of Arno, and they were sometimes analysed undiluted.

2.2. Apparatus

A Dionex Model 4500i ion chromatograph equipped with an autosampler, Dionex conductivity detector II, Spectra-Physics Model 4270 integrator, Perkin-Elmer Model 235 diode-array detector and Epson AX2e PC with Perkin-Elmer Omega software was used. The chromatographic conditions were as follows: mobile phase, 180 mM sodium carbonate–170 mM sodium hydrogencarbonate, 4.5 ml diluted to 1 l (conductivity 10–11 $\mu\text{S cm}$), pumped at 2 ml/min; regenerant, 25 mM sulphuric acid; regenerant flow-rate, 5 ml/min; loop, 20 μl ; and detection wavelength, 210 nm.

The ion chromatographic (IC) guard column and analytical column used were Dionex Ion Pac AG4A-SC (50 \times 4 mm I.D.) and Ion Pac As4A-SC (250 \times 4 mm I.D.), respectively.

Millipore Millex GS 0.45- μm syringe filters (25 mm) were used. A Millipore Milli-Q 50 water-purification system was utilized.

3. Results and discussion

The difficulties to overcome in the IC determination of nutrients in sea water arise from the high salinity of the samples, due to the especially high content of chlorides and sulfates, and from the comparatively low concentrations of the species of interest. On the one hand, high salinity makes it almost always necessary to dilute the samples, but on the other hand, the dilution can lower the concentrations of the analytes below the limits of detection, thus restricting the usefulness of the dilution itself. The concentration of nitrate ion in the samples is about two and four orders of magnitude lower than those of bromide and chloride, respectively. For this reason, when using conductometric detection, the peak of chloride tends to cover the adjacent peaks of bromide and nitrate, as shown in Fig. 1.

In Fig. 2 is instead shown the UV chromato-

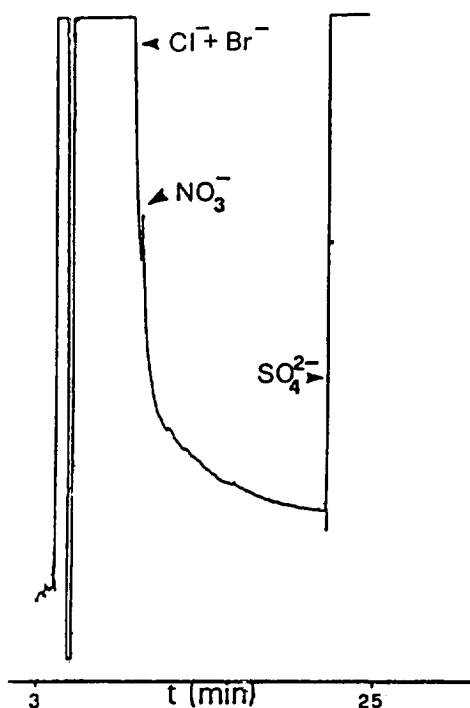


Fig. 1. Chromatogram obtained with conductimetric detection (range 0.3 $\mu\text{S cm}$) for a sample of sea water diluted tenfold.

gram at 210 nm of the same sample as in Fig. 1. UV detection removes the disadvantage of the interference of chloride, as its absorptivity is very low at the selected wavelength and it is therefore more suitable for the determination of nitrates in sea water.

To achieve a good separation between the peaks of bromide and nitrate, we diluted the concentrated eluent solution (180 mM sodium carbonate–170 mM sodium hydrogencarbonate) to a conductivity of about 10–11 $\mu\text{S cm}$. The mobile phase usually used in the analysis of fresh water is more concentrated (15–20 $\mu\text{S cm}$). For all the samples analysed, the separation between the peaks of bromide and nitrate was complete under the chromatographic conditions adopted, as shown in Fig. 2. Further, the comparison between the absorption spectra of nitrate in the standard solutions and in the samples and the values of the purity index of the related peaks

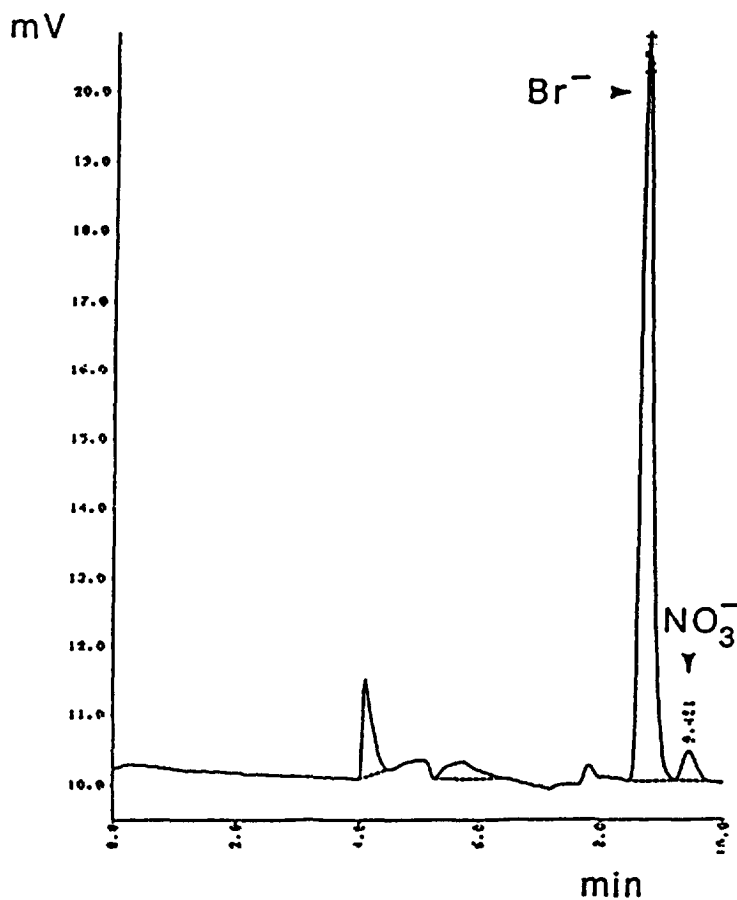


Fig. 2. Chromatogram obtained with UV detection for the same sample as in Fig. 1 ($\lambda = 210$ nm; nitrate concentration, $89 \mu\text{g/l}$; bromide concentration, $3.6 \mu\text{g/l}$).

indicated the lack of any interference in the analysis.

A good separation between the two peaks was also obtained with a more concentrated mobile phase, having a conductivity of about $20 \mu\text{S cm}$, pumped at 1 ml/min , but the retention times became longer and the shape of the peaks broadened.

The concentration of nitrate ion in the samples examined ranged from 0.3 to 11.1 mg/l . The minimum nitrate detectable concentration in sea water was 0.04 mg/l .

The samples taken at Calambrone nearly always showed the highest concentrations of nitrate, owing to the proximity to the mouth of the river Arno, which receives civil and industrial

wastes from a densely populated area and whose average flow is $99.3 \text{ m}^3/\text{s}$. The average value of the nitrate concentration (6.6 mg/l) is twenty times higher than that obtained for the same location in the period from August 1989 to September 1990 [1]. However, the period of that investigation was particularly dry and warm and the corresponding poor flow of the river could have reduced their supply of nutrients to the sea. The river supply, owing also to the morphology of the coast in this area, is a determinant factor. In fact, the trend of the values of salinity that were reported indicates that the slowly downward-sloping depth contour slackens the mixing between brackish and fresh water along the coast; the latter appears to slide over the former,

producing a poorly salty layer that is about 2 m deep and many miles long.

The concentrations of the soluble orthophosphate ion were evaluated by means of conductimetric detection. This kind of determination presented some difficulties. In fact, the limit of detection of orthophosphate by IC with conductimetric detection is $40 \mu\text{g/l}$ [2], which is 10–15 times higher than in the usual analytical methods based on molecular spectroscopy of suitable

derivatives [3,4]. Moreover, from a previous investigation [1] in the area of Calambrone, the average concentration of phosphate, measured all the year round, was found to be about $26 \mu\text{g/l}$, that is, lower than the limit of detection. Finally, the high salinity of the sample often prevented us from using adequate levels of sensitivity of the detector or made it essential to dilute the samples, with a further lowering of the concentration of this analyte. Therefore, the concentration of phosphate could be evaluated only in those samples which, despite the dilution, showed a concentration of phosphate higher than the limit of detection; the minimum phosphate concentration detectable in sea water was 0.1 mg/l .

Fig. 3 shows the peak of phosphate in the chromatogram of a sample characterized by a low level of salinity. The detectable values range from 0.3 to 1.6 mg/l of orthophosphate and are related to the Calambrone and Tre Ponti locations during the winter months, when the rainfall and the supply of nutrients by the streams are higher.

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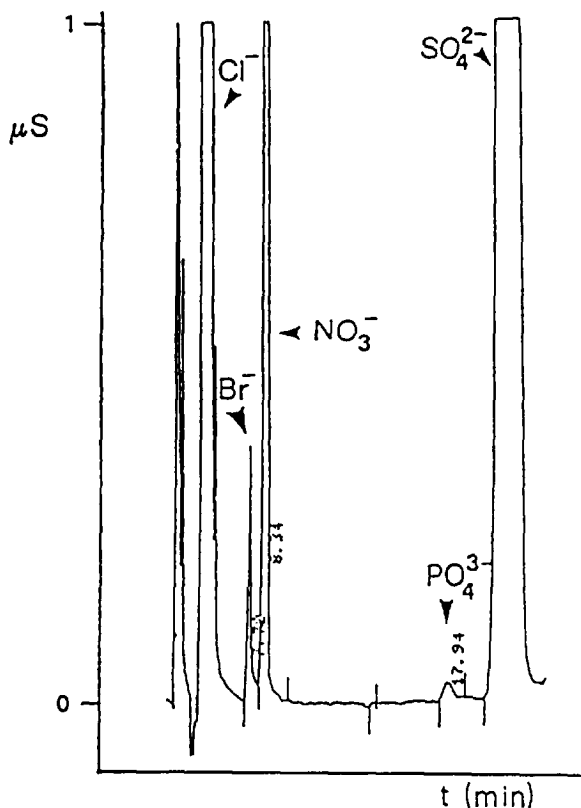


Fig. 3. Chromatogram obtained with conductimetric detection for undiluted sea water taken at Calambrone (range $1.0 \mu\text{S cm}$).