Determination of Nitrite, Bromide and Nitrate in Seawater Using Ion Chromatography

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The determination of low levels of inorganic ions in seawater samples with high salt content is challenging. Ion chromatography (IC) with suppressed conductivity and UV/Vis detection has the advantages of high sensitivity and selectivity for analysis of standard anions including fluoride, chloride, nitrite, nitrate, bromide, phosphate and sulphate. High linearity, low limits of detection as well as excellent precision of retention time and peak area were demonstrated using IC. The method was applied for analysis of nitrite, nitrate and bromide in seawater samples.

Introduction

Determination of inorganic ion concentration is important for water quality control. The quantity of nitric compounds especially has significant importance in shrimp and fish farming. Nitrite (NO_2-) is an intermediate product in bacterial nitrification and denitrification processes in the nitrogen cycle [1]. It appears as a result of feeding and can be highly toxic for aquatic animals, depending on the pH value. Nitrate (NO_3-) is a main nitrogen source for phytoplankton growth in seawater [2], and the normally constant bromide/chlorinity ratio is helpful to determine groundwater contamination as well as seawater intrusion.

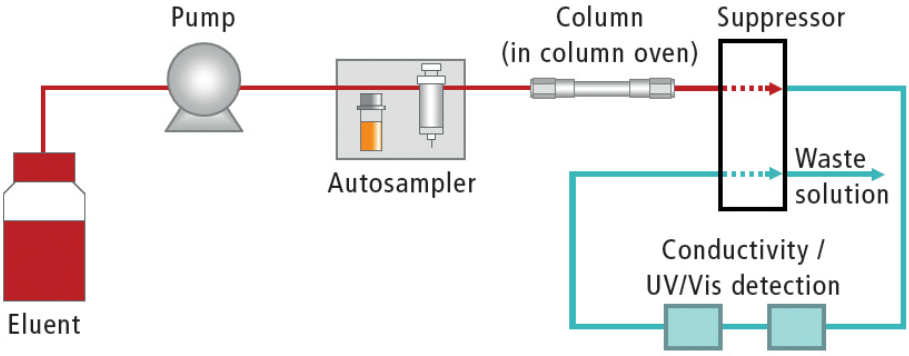

Figure 1: Flow diagram of the Shimadzu modular LC system.

For determination of nitrite and nitrate, many different techniques are reported [3]. Sensitive determination of traces of anions in samples with high salt content like seawater can be challenging. The ability of nitrite and nitrate as well as bromide to absorb UV light in the range around 210 nm in contrast to highly concentrated chloride is beneficial for analysis with required selectivity and high sensitivity by ion chromatography and UV detection [2,4].

The IC system with electrolytically regenerated suppression and UV detection provides sensitive measurements of anions in complex samples like seawater. In this work, standard anions including nitrite, nitrate and bromide were analysed by UV/Vis and conductivity detection after suppression of the eluent.

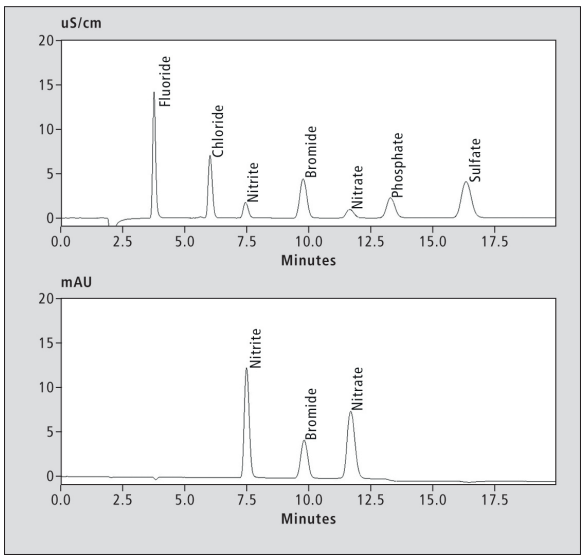

Figure 2: Chromatograms of seven standard anions, fluoride, chloride, nitrite, bromide, nitrate, sulphate and orthophosphate (top: suppressed conductivity; bottom: UV/Vis detection).

Experimental

The Shimadzu modular LC system consisted of a solvent delivery pump, autosampler, column oven and an electrolytically regenerated suppressor as well as conductivity and UV/Vis detectors (see Figure 1). Analytical conditions used are shown in Table 1.

Materials

The ultrapure water (ASTM Type 1) for preparation of the eluent and dilution of standards was prepared by arium® pro water purification system from Sartorius. Anions standards of fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulphate in water (1000 ppm, for IC) were purchased from Sigma Aldrich. Sodium carbonate (≥ 99.8%) and sodium bicarbonate (≥ 99.7%) for preparation of the eluent were purchased from Sigma Aldrich and Honeywell Fluka, respectively. Syringe filter (polyester, 45 µm pore size) for filtration of samples were purchased from Macherey-Nagel.

Table 1: Analytical conditions.

Column	Shim-pack IC-SA4 (150 mm L x 4.6 mm ID, 3.5 µm particle size)
Mobile phase	1.7 mmol/L sodium carbonate / 5.0 mmol/L sodium bicarbonate; pH 9.7
Flow rate	0.8 mL/min
Column temp.	50 °C
Injection volume	50 µL
Wavelength for UV detection	218 nm
Cell temp. of conductivity detector	Auto (53 °C)
Suppression	Electrolytically regenerated

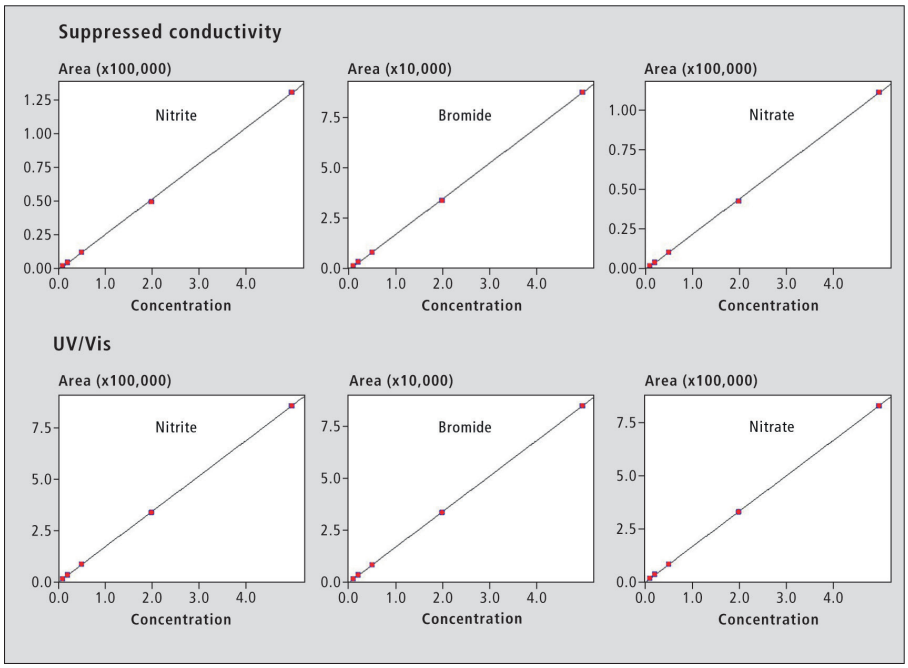

Figure 3: Calibration curves for standards of nitrite, bromide and nitrate obtained with suppressed conductivity and UV/Vis detection.

Table 2: Retention time and peak area reproducibility (n=5) for suppressed conductivity (all anions) and UV/Vis detection (nitrite, bromide and nitrate).

Anion	t_R precision (RSD [%])	Area precision (RSD [%])
Fluoride	0.03	0.03
Chloride	0.04	0.51
Nitrite	0.06 / 0.05	0.10 / 0.07
Bromide	0.06 / 0.06	0.06 / 0.20
Nitrate	0.07 / 0.06	0.08 / 0.06
Phosphate	0.04	0.21
Sulfate	0.06	0.12

Sample preparation

The seawater samples were diluted 1/20 (v/v) with ultrapure water and filtered through 0.45 µm PET syringe filters.

Results

Figure 2 illustrates conductivity and UV/Vis chromatograms for the separation of seven standard anions on a Shim-pack IC-SA4 column. Nitrite, bromide and nitrate show absorption in contrast to fluoride, chloride, phosphate and sulphate ions that were determined using conductivity detection. As listed in Table 2, all anions were determined within 17.5 min with high precision for retention time (RSD ≤ 0.07%) and peak area (RSD ≤ 0.51%) for both detectors.

Late eluting peaks might appear broad. The dispersion effect for late eluting anions is especially strong which is characteristic for isocratic elution. In addition, low kinetics of ion-exchange interactions limit high separation efficiency in ion chromatography.

Linearity and limit of detection

For both detectors, linearity in the calibration range of 0.1-5 ppm obtained with external standards (0.1, 0.2, 0.5, 1, 5 ppm) of nitrite, bromide and nitrate was excellent with a coefficient of determination of $R^2 \geq 0.9999$ (see Figure 3 and Table 3).

Limits of detection (LOD) were determined as signal to noise (S/N) ratio of 3.3. As shown in figure 3 and table 3, the LOD for nitrite and nitrate detected with UV/Vis detection (0.9 ppb and 1.4 ppb, respectively) were lower compared to suppressed conductivity (2.9 ppb and 4.8 ppb respectively). In contrast to nitrite and nitrate, bromide had lower LOD with suppressed conductivity (5.3 ppb) compared to UV/Vis detection (12.8 ppb).

Analysis of seawater

Figure 4 shows separation of anions in diluted seawater using suppressed conductivity and UV/Vis detection. In the samples, bromide and nitrate were determined. While both anions could clearly be detected by UV/Vis, nitrite concentration was below LOD by conductivity detection.

In three individually collected seawater samples, the concentration of bromide was determined (by UV/Vis detection) using the external calibration method in the range of 65.1 to 65.9 ppm. The nitrate concentration (UV/Vis detection) was significantly lower in the range of 0.5 to 1.3 ppm (semi-quantitative determination). Nitrite could not be identified in the 20x diluted sample. Peak tracking was also supported by spiking the dilution with 0.1 ppm nitrite, 2.5 ppm bromide and 0.1 ppm nitrate (Figure 5).

Conclusion

Ion chromatography with electrolytically regenerated suppression and conductivity as well as UV/Vis detection provides sensitive measurements of anions in complex samples like seawater. Due to the different selectivity and high sensitivity, both detectors can be applied complementarily for qualitative and quantitative analysis of anions.

Table 3: Calibration range, linearity and LOD for suppressed conductivity and UV/Vis detection. The LOD was calculated from a standard, applying the following formula:

Detection limit = Coeff x conc x N/S.

Anion	Calibration range [ppm]	Linearity	LOD [ppb] conductivity / UV
Nitrite	0.1-5	≥ 0.9999	2.9 / 0.9
Bromide	0.1-5	≥ 0.9999	5.3 / 12.8
Nitrate	0.1-5	≥ 0.9999	4.8 / 1.4

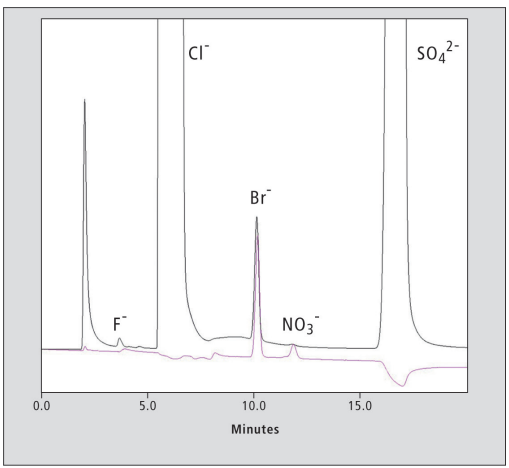

Figure 4: Suppressed conductivity (black) and UV/Vis (magenta) chromatogram of seawater diluted 1/20 (v/v) with water.

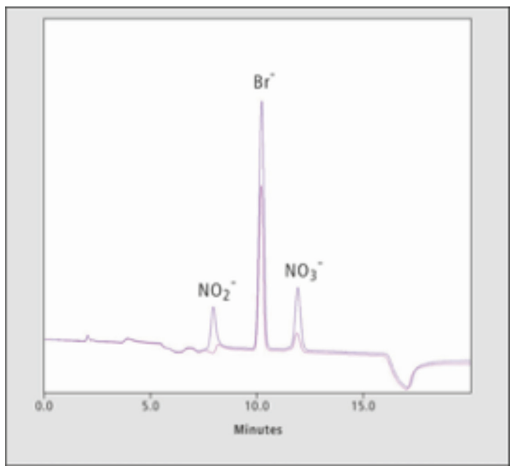

Figure 5: UV/Vis chromatograms of non-spiked (magenta) and spiked (black) seawater samples (diluted 1/20 (v/v) with water) with 0.1 ppm nitrite, 2.5 ppm bromide and 0.1 ppm nitrate.

References

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