Development of a Simple and Highly Sensitive Method for the Measurement of Nitrate and Nitrite in Seawater

Hitoshi Kodamatani, Takashi Tomiyasu

Kagoshima University

Summary

The concentrations of nitrate and nitrite ions in seawater are essential indicators for understanding the marine environment.   We have been developing an analytical system that separates these ions using a semimicro ion-pair chromatography (IPC) technique, converts them into peroxynitrite via UV irradiation at 222 nm (PR: photochemical reaction), and detects them through a luminol-based chemiluminescence reaction (CL).   This combined system is called IPC-PR-CL.   As part of the 2023 fiscal year outcomes supported by this grant program, we developed an IPC column by coating a graphite carbon narrow-bore column (2.1 mm i.d., 30 mm length) with cetyltrimethylammonium.   This enabled the separation and quantification of nitrite and nitrate ions within 3 minutes.   However, quantitative analysis of real seawater samples was not successfully achieved with this configuration.

To overcome this challenge, the present study utilized a commercially available narrow-bore ion chromatography (IC) column (2.0 mm i.d., 250 mm length) to ensure sufficient separation performance.   And then, we optimized the chemiluminescence detection cell and the photochemical reactor.   As a result, an IC-PR-CL system incorporating a 1.5 cm PFA tube (0.5 mm i.d.) for the CL detection cell and a 20 cm FEP tube (0.15 mm i.d.) for the PR reactor—corresponding to approximately 1 second of UV exposure time—was established.   Using an eluent flow rate of 0.25 mL/min, this configuration successfully enabled the detection of nitrate and nitrite ions in seawater samples.   The analysis time per sample remained unchanged from the previous system at 8 minutes, but the eluent consumption was reduced to one-fourth that of previous systems.   Under these optimized PR-CL detection conditions, we further explored the feasibility of converting the IC column to the IPC column and modifying the eluent composition to facilitate rapid analysis of seawater samples.   It was found that eluent components such as carbonate ions significantly affect not only chromatographic separation but also the PR-CL detection process.   Using the established semimicro IC-PR-CL system, we conducted measurements of nitrate and nitrite ions in seawater from three locations in Kagoshima Bay.   In particular, at a site known for active submarine hydrothermal venting, higher concentrations of nitrite and a notable decrease in nitrate concentrations were observed compared to other locations.   These results suggest that hydrothermal fumarolic activity may be responsible for the reduction of nitrate to nitrite.