Automatic Measurement of Dissolved Inorganic Nitrogen Ions in Coastal Field Using Simplified Flow Injection Method

Rei Arai, Koji Tada, Naoki Nakatani and Takeshi Okuno
Osaka Prefecture University, Osaka, Japan

Koichi Ohta
Toyota Motor Corporation, Aichi, Japan

Recently, the measurement of certain environmental factors such as dissolved oxygen and chlorophyll using electric sensors has been realized. Such measurement is continuous and automatic, and it is very important for the monitoring of the environment in coastal areas. However, it is difficult to continuously measure the chemical parameters because data must be obtained by chemical analysis. This paper introduces a simplified measurement system using absorption rate measurement of processed water by visible rays. The effectiveness of this method is demonstrated in field measurements in Osaka Bay.

INTRODUCTION

Since the 1960s, economic growth has caused an increase in the pollution of water around coastal areas in typical enclosed seas such as Osaka Bay. It has not yet been improved around urban coastal areas, despite considerable and varied research, because many kinds of wastewater, such as industrial and domestic wastewaters, contain high concentrations of nutrients, which can lead to various environmental problems, including red tide and anoxic water. In order to deal with these problems appropriately, it is important to continuously and automatically measure nutrient concentration with high resolution in time and space, thus providing a good understanding of coastal sea ecosystems.

In order to monitor nutrient concentration in the ocean, the measurement of dissolved inorganic nitrogen (DIN) is most important. It is classified into nitrate (NO$_3^-$), nitrite (NO$_2^-$) and ammonia ions (NH$_3^+$), all of which are analyzed in a laboratory. Since we have to collect discrete samples or use research vessels with onboard facilities, it is difficult to measure in detail the fluctuation of nutrients in time and space. In order to eliminate such problems in the conventional measuring of DIN, its automatic in-situ measurement should be developed for monitoring the marine environment.

Spectrometry is very effective for measuring chemical matter concentration without any chemical treatment. Since nitrate and nitrite ions show particular absorption decay of radiation in the ultraviolet range wavelength, as discussed by Armstrong (1963), spectrometry has been used for many years to monitor nitrate in fresh water. With regard to seawater, it is very difficult to measure nitrate and nitrite concentrations because of the presence of high-concentration bromide included in the seawater. In order to measure the summation of nitrate and nitrite (DINOx), in 2008 we proposed a new method that determines DINOx concentration using a spectra model of seawater in the ultraviolet (UV) region. This method is most effective for determining the distribution or vertical profile of DINOx concentration because of its high response speed. However, this method cannot measure ammonia ions that do not show an absorption characteristic in the UV region. It is not appropriate to neglect the ammonia concentration since ammonia is generally one of the main components of DIN involved in the growth of phytoplankton in coastal seas.

Alternatively, flow injection analysis (FIA) is very effective for continuously measuring all kinds of chemical matter. Its concept was conceived by Jaromir et al., whose first paper on the subject appeared in 1975. We have already (2004, 2006) developed a specific instrument for measuring the nutrient concentration of seawater and have shown its effectiveness when applied to nitrite ion. Johnson et al. (1986, 1989, 1994) developed an in-situ instrument using FIA and used it to measure nitrate and nitrite ion concentrations at over the 2000-m depth. David et al. (1998, 1999) measured nitrate, nitrite and ammonia ion concentration in seawater using FIA with fluorescence detection, which provides precise measurement at low concentrations (nmol/L). These remarkable results indicate it is possible to determine many kinds of matter, not only nitrate, nitrite and ammonia ions but also phosphoric, silicic acid and iron ions, using FIA in coastal seawater. In these FIA methods, the measurement systems consist of many parts: the reactive part, channel, pump and so on. If we try to measure the many kinds of matter in seawater simultaneously, it is necessary to prepare the same number of measurement systems as measuring items. FIA is thus not a suitable method for in-situ measurement because the mechanism of the measurement equipment is assumed to be extremely complex and large. In order to realize measurement with excellent temporal resolution of fluctuating nitrogen in seawater, only DIN should be measured, rather than measuring the respective components of nitrate, nitrite and ammonia simultaneously.

In this study, we have developed a reduction column containing copper-zinc grains as well as a new analysis method so that the FIA system can be used for measuring DIN in seawater. By means of this column reducing nitrate and nitrite to ammonia, we can obtain the DIN concentration in seawater at one time. This system is very simple and portable, creating a robust and practical method suitable for the automatic measurement of DIN in the field. The obtained results in a typical coastal sea environment show the variation in DIN in detail as well as the method’s effectiveness.