

Measuring Instrument for Dissolved Inorganic Nitrogen and Phosphate Ions

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It is important to conduct continuous and automatic measurements of nutrients in seawater, such as dissolved inorganic nitrogen and phosphoric and silicic acid ions, for monitoring the environment in coastal areas; however, such continuous measurements are difficult because the data must be obtained by chemical analysis. This paper introduces a simplified measurement instrument that uses absorption rate measurements of filtered seawater in the visible range. We have estimated the uncertainty in the nutrient measurements and verified the accuracy of our instrument. Further, the effectiveness of this method has been demonstrated by field measurements in Osaka Bay.

INTRODUCTION

In coastal sea areas, wastewater carrying high concentrations of nutrients and organic matter often flows into the seawater, leading to the so-called eutrophication phenomenon. Eutrophication refers to increases in nutrient concentrations that may cause dense phytoplankton growth. In coastal waters, eutrophication causes various environmental problems, such as red tide and anoxic water. In order to deal with eutrophication and its related problems appropriately, it is important to continuously and automatically measure the nutrient concentrations with high resolution in time and space, since this will provide a good understanding of the current status of coastal sea ecosystems.

In particular, the measurements of nutrients such as dissolved inorganic nitrogen (DIN), which comprises nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+) ions, and orthophosphoric acid (PO_4) and silicic acid ions are extremely important because they are useful for understanding the specific behaviors of the primary production of phytoplankton. DIN and phosphoric and silicic acid ions are typically analyzed in laboratories. However, it is difficult to measure the nutrients automatically; also, as discrete samples collected by research vessels with onboard facilities have to be used, it is difficult to obtain detailed measurements of the fluctuations in nutrients in time and space.

Degobbi et al. (2005) and Zou et al. (2001) have analyzed many seawater samples and strongly expressed the need for in situ measurements of nutrients. Gallegos et al. (1992) indicated that the in flow of nutrient-rich waters into coastal seas due to storms can have significant effects on primary productions. This implies that monitoring schemes in which only a few samples are collected can fail to identify transients, such as those present during storms—events that occur over a matter of hours. In order to eliminate such problems in the conventional measurements of DIN and PO_4 concentrations, which are required for monitoring marine environments, automatic in situ measurements should be developed.

Spectrometry in the ultraviolet (UV) wavelength range is extremely effective for measuring chemical concentrations without any chemical treatment. Also, as nitrate and nitrite ions show particular absorption decays of radiation in the UV wavelength range, as discussed by Armstrong (1963), spectrometry has been used for many years to monitor nitrates in fresh water. In the case of seawater, it is very difficult to measure the nitrate and nitrite concentrations from the presence of high-concentration bromides and dissolved organic matter in seawater. Johnson et al. (1986) and Plant et al. (2009) have reported the successful application of a high-resolution in situ UV spectrometer (ISUS) to measure the nitrate concentrations in depth profiles in oceans. In 2008, we proposed a new method that determines DINOx concentrations using a spectra model of seawater in the UV region. This is the most effective method for determining the distributions, in terms of vertical profiles of DINOx concentrations, because of its high response speeds. However, ammonia and phosphorus ions that do not show absorption characteristics in the UV region cannot be measured using this method, and it is not appropriate to neglect these ions since they are generally among the primary components in the growth of phytoplankton in coastal seas.

Alternatively, flow injection analysis (FIA) is also an extremely effective technique for continuously measuring all types of chemical matter. The FIA concept was conceived by Jaromir et al., whose first paper on the subject appeared in 1975. The technique rapidly captured the imagination of analytical chemists and is well known in such areas as process and industrial chemistries, pharmaceuticals and biochemistry. In 2004, we developed a specific instrument for measuring the nitrate concentrations of seawater, and we have shown its effectiveness when applied to nitrite ions. Johnson et al. (1986, 1989, 1994) developed an in situ instrument using FIA and used it to measure the nitrate and nitrite ion concentrations at a depth over 2 km. David et al. (1998, 1999) measured the nitrate, nitrite and ammonia ion concentrations in seawater using FIA with fluorescence detection; this technique provides precise measurements at low concentrations ($\mu\text{mol/L}$). These remarkable results indicate it is possible to determine many types of matter—not only nitrate, nitrite and ammonia ions but also phosphoric acid, silicic acid and iron ions—using FIA in coastal seawaters. However, in these methods, the measurement systems comprise many parts, such as the reactive part, channel and pump. If we attempt to measure many types of matter in seawater simultaneously, it is necessary to use the same number of

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