Automatic and Continuous Measurement of Nutrient at Coastal Field

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Some of the environmental factors such as dissolved oxygen, chlorophyll, turbidity and so on can be measured by electric sensor recently. It enables to measure these continually and automatically. This kind measurement is very important for monitoring of the environment of coastal area. However, since it is difficult to measure the chemical parameter continuously because of its reaction time, the so-called batch type analysis has to be employed. In order to monitor the nutrient in ocean, the measurement of dissolved nitrogen is most important because it is useful for understanding a particular behavior of the phytoplankton as the primary production. In this paper, the method of absorption rate measurement of processed water by the visible ray is described. The water is drawn through pipe by a tube pump and processed with a reagent. After the chemical reaction through mixing coil, the absorption rate is measured by electric sensor continuously. The effectiveness of the present method is shown in the field measurement in Osaka Bay.

Keywords: Monitoring System, Continuous Measurement, Nutrient, Flow Injection

1. Introduction

Recently, many important factors for environment such as dissolved oxygen, chlorophyll, turbidity and so on can be measured by electric sensor. It enables to measure these continually and automatically. It is very important to develop a particular sensor for the continuous measurement and for monitoring the environment in the coastal area. However, since it is difficult to measure the chemical parameter continuously because of consuming time for the chemical reaction, the so-called batch type analysis is always employed. We have to collect discrete samples or use research vessels with laboratory.

In order to monitor the nutrient in ocean, the measurement of dissolved inorganic nitrogen (DIN) is most important because it is useful for understanding a particular behavior of the phytoplankton as the primary production. It is classified to ammonia, nitrate, and nitrite. The authors have tried to develop a practical device for the measurement of these at coastal field.

Several techniques, such as an ion chromatography, fluorescence analysis method and so on, can be used for this kind of measurements. In this research, the authors have decided to employ the method of absorption rate measurement of processed water by conventional photometry with visible ray. The water is drawn through pipe by a tube pump and processed with a reagent. After the chemical reaction through mixing coil, the absorption rate is measured by electric sensor continuously.

The several measured results are shown and explained the physical phenomena of coast of Yura, typical enclosed sea, and Rinku Park, an artificial lagoon.

2. Nutrient in Seawater

Generally, it is well known that the phytoplankton plays an important role in a primary production in seawater. In this stage of Food Chain, inorganic compounds of nitrogen and phosphorus are most essential element.

The nitrogen in the sea occurs in many forms that are not easily converted from one another. These in-
clude dissolved molecular nitrogen (N₂) and the ionic forms of ammonia (NH₄⁺), nitrite (NO₂⁻), and nitrate (NO₃⁻), as well as organic compounds such as urea (CO(NH₂)₂). The dominant form of nitrogen in the ocean is the nitrate ion, and it is often this form that is taken up by phytoplankton, although many species can also utilize nitrite or ammonia.

Dissolved organic nitrogen (DON) and particulate organic nitrogen (PON) both serve as nutrient for growth of phytoplankton. Bacteria break down proteins to amino acids and ammonia, and the later is oxidized in the nitrification process. The eventual release of dissolved inorganic nitrogen (DIN) makes three forms available again for uptake by the phytoplankton. The various types of bacteria involved in this cycling can themselves serve as a direct source of food for some nano- and microzooplankton.

Main purpose of this research is the measurement of DIN in order to investigate the ecological and biogeochemistry of aquatic ecosystems.

3. Measurement Method for Nutrient

In order to analyze the sampled water in laboratory, many measurement methods have been developed already. In these methods, several methods are selected for an investigation in view of automatic and continuous measurement, in-situ measurement.

3.1 Principle of measurement

Dominant two methods can be selected in these methods in terms of sensor type. One is the absorbed rate measurement method and the other the potential difference method.

The former is the method using the fact that the absorbed rate through the sampled water should be proportional to the pass length and concentration of the water\(^{1,2}\). This luminance through the water can be expressed by Beer-Bouguer-Lambert principle. Equation (1) shows its rate, \( T \).

\[
\begin{align*}
T &= I/I_0 = 10^{-\epsilon bc} \\
A &= -\log(I/I_0) = \epsilon bc
\end{align*}
\]  

where \( I \) shows the penetration ray strength, \( I_0 \) the inlet ray strength, \( b \) the pass length, \( c \) the concentration of the sampled water, \( \epsilon \) the empirical constant which should be determined by characteristic material, temperature, wave length of the ray and so on. \( A \) is called absorbed rate. If the wavelength of the light source is known, the concentration of the water can be evaluated by the measurement value of absorbed rate.

On the other hand, the potential difference method of electro sensor is always used in pH meter. It consists of glass and other reference electrode. The potential difference gives the concentration. The difference is expressed by Nernst equation as follows:

\[
oX + ne^- \rightarrow bRed
\]  

\[
E = E^o - \frac{2.3026RT}{nF} \log \frac{[Red]^b}{[Ox]^n}
\]  

where \( Ox \) shows the oxide and \( Red \) the deoxidation. According to this principle, the following practical method can be available.

3.2 Absorption photometry by multi wavelength ray

Generally, it is difficult to determine the nutrient by using mono-wavelength because the seawater always includes dissolved organic material (DOM), particulate organic material (POM) and also particulate inorganic material (PIM). These show the difference absorbed rate \( \epsilon \) against to the various wavelength \( \lambda \).

If we choose one particular wavelength, the absorbed rate can be expressed in the following equation.

\[
A_\lambda = \sum_{j=1}^{n} A_{\lambda j} = b \sum_{j=1}^{n} \epsilon_{\lambda j} c_j
\]  

Therefore, in the case of multi-wavelength ray, the following algebraic equation can be obtained.

\[
A_i = be_{\lambda i} c_j \quad (i, j = 1, 2, \ldots, n)
\]  

The unknown concentration \( c \) can be determined by this equation as many people use the similar technique in remote sensing with a satellite.

Of course, ones can use not only visible ray but also ultraviolet rays. In the case of the later one, ultraviolet laser, some of the different possibilities would be appeared because of his high energy level of the laser. The ionic forms of nitrite (NO₂⁻) and nitrate (NO₃⁻) absorb the ray much during the wavelength range from 220nm to 230nm.\(^3\) In this range, it is possible to ignore the absorbed rate of the water itself. It is very useful for the accurate measurement of the nutrient.
3.3 Absorbed rate measurement using reagent

If we use visible light to measure the three forms of nitrogen, the sampled water should be colored by a particular reagent, because these three forms do not absorb the light in the range of visible ray much. It is easy to treat the colored water for the measurement. The particular reagent makes chemical process of the sampled water with the ionic forms of ammonia (NH₄⁺), nitrite (NO₂⁻), and nitrate (NO₃⁻). This method would be a practical one because of its simple process of analysis. The method will be discussed in detail later.

3.4 Electrode for selected ion

It is possible to develop a special electric sensor with glass film of porous material, which shows generation of electricity. It is determined by density of the sampled water. The electrode will respond to the particular ion selectively. This would be an interesting feature to develop a new sensor in the future.

4. Mechanics for Measurement

It is well known ion chromatography method and flow injection method for the automatic measurement of the analysis in the laboratory. We should examine the possibility of using these methods in the coastal field as the in-situ measurement.

Ion chromatography method is accurate technique for determine the various ion material quantitatively. It consists of three parts, the column for separate the mixed material, the high pressure pump for making flowing out the water, and also the sensor for measurement of density of the sampled water. This method is the technique, which uses the time difference of chemical process of ion in the column of separating the ingredient. It is very difficult to use this principle for the field measurement, owing to its large size of the machine. This would be a disadvantage in the measurement. It causes the necessary of batch type analysis. This means that it is not suitable for the in-situ measurement.

On the other hand, the flow injection method is known as a method without column for separating the component, but as the analysis method in the flow of the sampled water[1]. It is possible to analyze continuously in the flow of the water. This is big advantage for this research.

The examined results of the several methods mentioned in above section are summarized in Table 1. From the view point of the continuous measurement, the so-called real time measurement, the method with reagent, which is used for coloring water, is not suitable because of the consuming time for chemical process. However, it shows advantage for the analysis of seawater because it includes the strong interfere ion such as sodium, chlorine and so on. It is difficult to measure the particular ion of seawater by the ion-chromatography method.

In order to measure the density of the colored sampled water, the visible light can be easily used. It is known that the accuracy of this method is not so high, but it enables to measure continuously the water as a flow. The mechanism is not complicated and it can be manufactured with compact small size.

Consequently, the flow injection method with the reagent, which colors the water, is employed here for the measurement method of the nutrient. Fig. 1 shows the measuring system developed here. The seawater is drawn by tube pump, which makes very slow flow
with sampled water, and the reagent is also drawn by the tube. This quantity should be very accurate and stable of course there are mixed in the mixing coil, a kind of spiral tube. The colored water is transferred into quartz cell and measured its density by absorption photometry. The output signal is analyzed and processed as the digital data.

5. Measurement Results

The nitrite ($\text{NO}_2^-$) is measured continuously at Yura, in Awaji Island and also in a artificial lagoon where is in the Rinku-Park near Kansai International Airport.

Fig. 2 shows the map of Osaka Bay. Yura is located at southern part of Osaka Bay, and also in Awaji Island. Yura is a small enclosed-sea, where is similar to the Osaka Bay. It has two mouths, Shin-kawa-guchi and Ima-gawa-guchi. The length is around 2.5km from north to south and 1.5km from west to east.

At Shin-kawa-guchi, north mouth of the channel, the nitrite ($\text{NO}_2^-$) was measured continuously two hours in November 23rd, 2002. At the same time, seawater has been sampled every one hour and analyzed it by conventional method at laboratory.

As the measured result is shown in Fig.3, the measurement values by the present method is close to the results by conventional analysis. Since the small fluctuation of the output data must be the result of noise owing to the measuring system, it should be filtered with low frequency passed. However, the detail of the suitable analysis is not known at the moment. This figure shows the real output to understand the system. It can be said that it shows the great possibility of the further measurement in the field, in case of much change due to tide and so on. There is not much change at the mouth on this day. However it must has good advantage for the investigation of the change of nutrient with time dependency or flow dependency in the future.

The other measurement was made at Rinku-Park, where is located the opposite side of Awaji Island, near the Kansai International Airport as shown in Fig.4. An artificial lagoon, shown in Fig.5, is in the park for the purpose of water purification. By the long-term investigation, a lot of the phenomenon in the lagoon...
is clarified already. But the change of nutrient has not been measured of course owing to the difficulty of the measuring.

The lagoon is build by pebble stone. The size of the lagoon is around 120x50m. One side of the lagoon is connected outside sea, Osaka Bay, through embankment. The measurement was made near the embankment because the fresh seawater flows into the lagoon according to the tide. Not only nutrient but also dissolve oxygen, temperature, and also sea level due to tide are measured. These are shown in Fig.6.

The measured results show clearly the change at 16:00 and more lately with tide and flow. It is known that the outside rich water flows into the lagoon due to the tide. The measured results shows that it is coincide to this phenomenon.

6. Conclusions

This paper deals with the development of a new measuring system that enables to measure the nutrients automatically and continuously in the field of the coast.

Several methods are examined in detail and it is found that the absorbed rate measurement method with reagent for coloring has good advantage, and it was developed. The present method is of the flow injection technique.

The measured results show good agreement with the conventional analysis ones, which are obtained in
a laboratory by the batch type analysis. The continuous measurement would be an interesting method to investigate the temporal change and its effects.

References


