

Feature Article

Application

Ammonia Nitrogen Monitor HC-200NH

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Because the electric power for the air blower to be used for the aeration tank on sewage plant is large, an adequate blower control with ammonia nitrogen concentration is expected. The ion electrode method enables continuous measurement. However the instability of the ion electrode method often is an issue for applying the process control. The cause of the instability is that the inner solution of ion electrode is diluted. The control of the osmotic pressure of the inner solution prevents diluting inner solution. The prototype was installed in a sewage water plant for a long term stability test and stable measurement was confirmed.

Introduction

The earth is said to be rich in water of approximately 1.35 billion km³ as it is also called the “watery planet”. However, more than ninety nine percent of it is seawater and most of fresh water exists in the form of glaciers and groundwater. Therefore, the amount of water accessible to humans such as river and lake waters is as small as a hundred thousand km³, accounting for only about 0.01% of the water on the earth.^[1] To make effective use of limited water resources, a proper effluent treatment is essential. Treating used water resources properly enables to return them to the water environment and to take the water again from that environment for use. On the other hand, a large amount of energy is consumed in the effluent treatment process, resulting in the emission of greenhouse gases. Reducing consumption energy without losing the quality of effluent treatment is considered one of the important issues.^[2, 3] For example, in Tokyo, approximately 40% of the greenhouse gases emitted through the Tokyo metropolitan government’s business activities are emitted by the Bureau of Sewerage, and approximately 44% of which are due to electricity usage. In particular, the air blowers which feed the air to the aeration tanks required for sewerage treatment consume as much as approximately 30% of the electricity used at the water reclamation center.^[3] In the aeration tanks, the organic constituents are degraded and removed microbially, and the air (oxygen) is supplied from the air blowers to activate biological reaction. If the amount of

air supplied by the air blowers is larger than the load, the treatment efficiency is reduced. On the other hand, if it is smaller, the treatment water quality is decreased. In some reclamation centers, the air blow volume is controlled based on the dissolved oxygen level because the treatment condition is linked to the dissolved oxygen level. However, the target dissolved oxygen level must be kept high in order to keep the effluent quality. Therefore, there is considered to be still room for improvement.

For this reason, the control using the ammonia nitrogen concentration as an index is currently studied and put to practical use by many companies and local authorities.^[3-5] Since the aeration tanks are intended to degrade and remove ammonia nitrogen, it is said to be able to control more efficiently by monitoring the ammonia nitrogen concentration that is a direct index. HORIBA group has newly developed HC-200NH ammonia nitrogen concentration meter for aeration tanks as one of the H-1 series. For more than 60 years, HORIBA group has developed various kinds of ion meters including the pH meter which is our first product. HC-200NH was developed based on the technologies we have accumulated for a long time and it enabled more stable measurement than conventional meters. In this document, the explanation of the principle of ion electrode method which we newly developed and the examples of actual sample measurements using HC-200NH are introduced.

Table 1 Measurement methods of ammonia nitrogen

Name	Merits	Demerits
Ion electrode method	Reagents are not necessary. Good for real time measurement.	Short interval of replacement. Unsteadiness of sensor.
Spectrometric method (JIS K 0400-42-60)	Few of interference influences.	Coloring reagents are necessary. Waste liquid treatment are necessary. Real time measurement is difficult.
Potentiometric method (JIS K 0400-42-80)	Few of interference influences.	Alkalinizing reagents are necessary. Waste liquid treatment are necessary. Real time measurement is difficult.

Features of HC-200NH

External appearance and configuration

Figure 1 shows the external appearance of HC-200NH. A sensor is fixed to the transmitter. To the sensor, an ammonium ion, potassium ion and reference tips are fixed. The potassium ion tip is for correction of ammonium ion concentrations. Since these tips are replaceable, it is not required to replace all tips together and respective tips can be replaced individually if any of them is deteriorated, leading to the reduction of running cost. In addition, just tightening the sensor cap enables to mount three tips at once without using any dedicated tool. Although not shown in the Figure, a sensor holder and a pole stand, etc. are required for retaining the sensor when installing this meter. An ultrasonic or air jet scrubbers can be combined with the sensor as needed, which may be effective to increase the maintainability. In addition, using DO-2000 optical dissolved oxygen sensor as an option enables simultaneous measurement of ammonia nitrogen and dissolved oxygen. This meter has a configuration which is more suitable for air volume control, because both items can be measured with a single meter.

Measurement principle

In general, there are several kinds of methods for measuring the ammonia nitrogen concentration as shown in Table 1. In controlling the air volume in aeration tanks, an ability to perform continuous measurement, an ability to immerse directly in the tank and the use of no reagent in measurements are preferred. Since both

absorptiometric and potentiometric methods are associated with chemical reaction, it is difficult to perform continuous measurement. As a result, the device used for the measurement needs to be sampling type and reactive reagent is required^[6, 7]. Since the ion electrode method satisfies these conditions, it is considered to be suitable for the air volume control in aeration tanks. However, the conventional meters based on the ion electrode method had problems with the use for continuous measurement purposes such as short electrode life and lack of stability, etc. In the development process of this product, we found out the primary cause of these problems was the dilution effect of internal solution and adjusting the osmotic pressure of the internal solution enabled stable measurement (patent registered).^[8]

Figure 2 shows the outline figure of the principle of ion electrode method. The electro motive force generated between the ion electrode and reference electrode is measured to convert into concentration. An ion electrode consists of an ion selective membrane, an internal solution, an internal electrode and a casing, etc. The selective membrane is a specific type of membrane which reacts to ammonium ions selectively. When the selective membrane is immersed in a sample, an electro motive force according to the ion concentration difference between the sample and the internal solution is generated. On the other hand, a reference electrode shows constant electrical potential regardless of ammonium ion concentration.

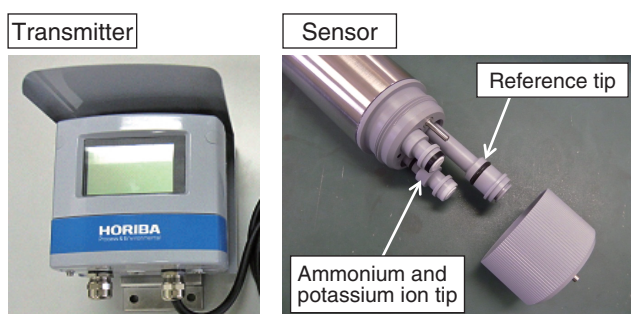


Figure 1 HC-200NH

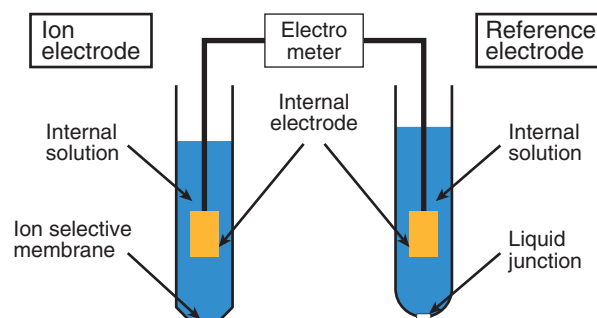


Figure 2 Principle of ion electrode method

The relationships of ion concentration and electro motive force are known to follow Equation 1 and 2.

$$E = e + S \times \log \frac{a_{\text{NH}_4^+, \text{S}} + k \times a_{\text{K}^+, \text{S}}}{a_{\text{NH}_4^+, \text{I}}} \dots\dots\dots (1)$$

$$S = 2.3 \times \frac{RT}{F} \dots\dots\dots (2)$$

However, if the interference effect is apparently negligible, Equation 1 can be considered to be equivalent to Equation 3. To simplify the discussion, Equation 3 is used in the following.

$$E = e + S \times \log \frac{a_{\text{NH}_4^+, \text{S}}}{a_{\text{NH}_4^+, \text{I}}} \dots\dots\dots (3)$$

Where, E is an elective motive force, e is an asymmetry potential difference^{*1}, S is sensitivity^{*2}, $a_{\text{NH}_4^+, \text{S}}$ is ammonium ion activity in sample, $a_{\text{K}^+, \text{S}}$ is potassium ion activity in sample, $a_{\text{NH}_4^+, \text{I}}$ is ammonium ion activity in ion electrode internal solution, k is a selectivity coefficient, R is a gas constant, T is absolute temperature and F is a Faraday constant. Since sensitivity is temperature dependent as Equation 2 shows, an elective motive force is also temperature dependent. When $a_{\text{NH}_4^+, \text{S}} = a_{\text{NH}_4^+, \text{I}}$ the second term of Equation 3 is always zero and E shows a constant value as $E = e$ regardless of temperature. Such point is called an “isothermal point”. Designing the isothermal point within the measurement range is required to reduce the temperature compensation error small.

*1: Asymmetry potential difference is an electro motive force generated when the both selective membrane-mediated sides have the solutions with the same ammonium ion activity. It is expected to be 0 mV under ideal conditions. Since it may practically change depending on manufacturing variations and deterioration state, it needs to be adjusted through the calibration of reference solution, etc.

*2: Sensitivity shows a change in an electro motive force when the logarithmic value of ammonium ion activity in a sample ($\log a_{\text{NH}_4^+, \text{S}}$) is changed by a single unit, that is, the activity is changed by ten times. Under ideal conditions, it is expected to be 59.40 mV at 25 degree Celsius. Since it may practically change depending on manufacturing variations and deterioration state, it needs to be adjusted through the calibration of reference solution, etc.

Improvement of the stability of ion electrode

As described above, there is a stability problem in using an ion electrode in industrial continuous applications, which is mainly caused by the dilution of the ion electrode internal solution. The mechanism of the problem is following.

The selective membrane of many ion electrodes is flexible

polyvinyl chloride resin made by mixing polyvinyl chloride resin with plasticizing agent and ion responsible compound. When the concentration of the solute material in the internal solution is higher than that in a sample, moisture penetrates into the internal solution side due to osmotic pressure difference. It is clear from Equation 3 that E increases when $a_{\text{NH}_4^+, \text{I}}$ decreases. However, a decrease of $a_{\text{NH}_4^+, \text{I}}$ is not assumed but an increase of $a_{\text{NH}_4^+, \text{S}}$ is assumed, because $a_{\text{NH}_4^+, \text{I}}$ is the designed value and calculations are done based on the designed values. Therefore the dilution of the internal solution during continuous measurement leads a measurement error on the positive side.

Diluting the internal solution enables to adjust the osmotic pressure. On the other hand, the isothermal point goes out of the measurement range, resulting in a large temperature compensation error. Although the chloride ion activity value is commonly considered to be the same between an ion electrode internal solution and a reference electrode internal solution, we reviewed of this conventional rule and leaded Equation 4.

$$E = e + S \times \log \left(\frac{a_{\text{NH}_4^+, \text{S}}}{a_{\text{NH}_4^+, \text{I}}} \times \frac{a_{\text{Cl}^-, \text{R}}}{a_{\text{Cl}^-, \text{I}}} \right) \dots\dots\dots (4)$$

Where, $a_{\text{Cl}^-, \text{R}}$ is the chloride ion activity of a reference electrode and $a_{\text{Cl}^-, \text{I}}$ is that in an ion electrode internal solution.

Since $\frac{a_{\text{Cl}^-, \text{R}}}{a_{\text{Cl}^-, \text{I}}} = 1$ is generally considered to be 1, it is omitted in Equation 3. However, including this part allows free design of the isothermal point and the osmotic pressure of the internal solution.

Performance and measurement examples

Stability of the newly-developed sensor

The effect of adjusting the osmotic pressure of the internal solution was investigated. A sensor which was adjusted and the one which was not adjusted were immersed continuously in a simulated sample solution of 40 degree Celsius to investigate changes in electro motive force. Figure 3 shows the results. The sensor which was not adjusted indicated changes of +27 mV in 100 days on average. On the other hand, the sensor which was adjusted was confirmed to indicate changes of -3.9 mV on average. As a result of checking the external appearance of the tips, the swelling of the membrane due to an increase in the internal solution volume was observed on the sensor which was not adjusted.

Response time

Response time is important because the air volume

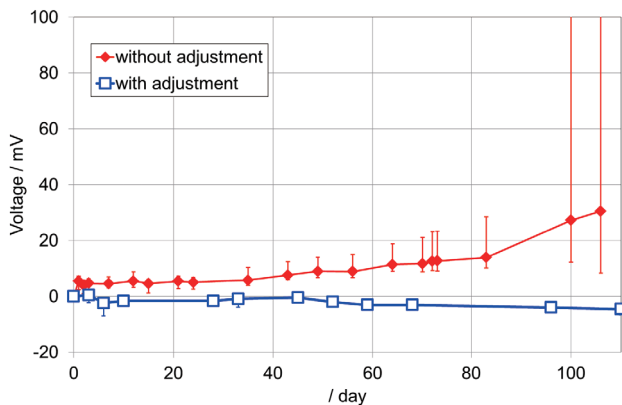


Figure 3 Voltage change of two type sensor immersed in 40 deg C test solution. ◆ is without adjustment and □ is with adjustment. Error bar shows maximum and minimum values of n = 10 sensors.

is controlled in aeration tanks according to the ammonia nitrogen concentration. There are considered to be two cases of the inconveniences caused by the delay in response. In the reduction phase of the ammonia nitrogen concentration, an excessive aeration may be occurred. The situation gets worse in the increase phase, where the treatment water quality may be reduced due to insufficient aeration. The response time is generally required within ten minutes. Figure 4 shows the response of HC-200NH in a standard solution. As a result of replacing the standard solution from the one of 1 mg-N/L with the one of 10 mg-N/L, it was confirmed that the reading became stable within three minutes and HC-200NH had sufficient responsiveness in controlling the air volume.

An example of a measurement in the field

HC-200NH is tested in several fields. An example, the result of the test conducted in a sewerage treatment plant for more than two years will be introduced below. As Figure 5 shows the test scene, DO-2000, a sensor holder and an ultrasonic scrubber were used in combination. During the test period, the manual analysis data based on

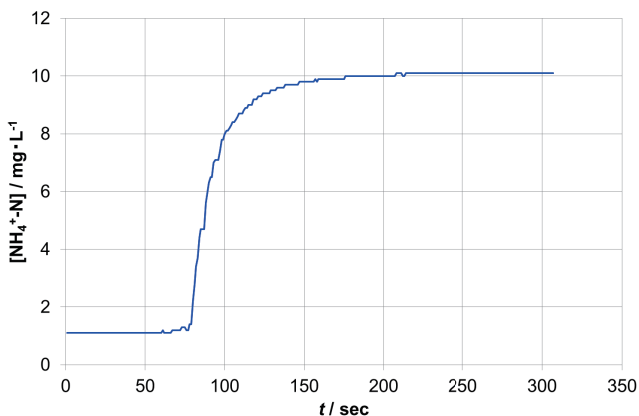


Figure 4 Response of HC-200NH in standard solutions (1 mg-N/L and 10 mg-N/L).



Figure 5 Field test on sewerage treatment plant

the potentiometric method and the readings of HC-200NH are compared and checked on a daily basis.

Figure 6 shows a measurement example. The readings of ammonia nitrogen concentrations were confirmed to be in good agreement with the potentiometric method. There was observed a circadian variation in ammonia nitrogen concentration which had a tendency to increase from the evening to the midnight and decrease in the morning. This is because people's activities at home increase from the evening and reflects the change in the load which is actually applied to the sewerage treatment plant. There was also observed a relationship of ammonia nitrogen concentration and rainfalls. After it was rain over 10 mm per day, the ammonia nitrogen concentration decreased and dissolved oxygen concentration increased. It is indicated that excess aerations were occurred after the rain.

Conclusion

HORIBA group developed HC-200NH, an ammonia

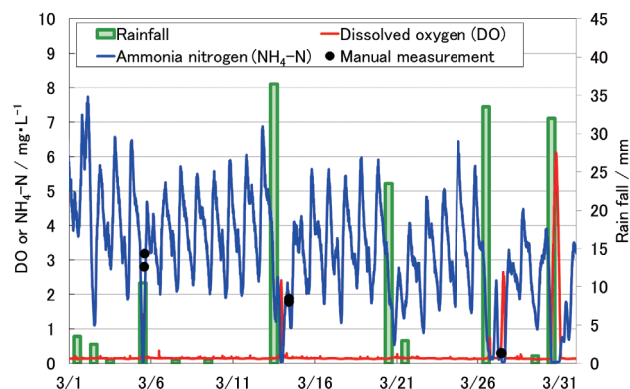


Figure 6 Example of field test data

nitrogen concentration meter for aeration tanks this time. Through the development of this system, we also developed our concentration measuring technology based on the ion electrode method we have cultivated over sixty years. This system is expected to contribute not only to the proper air volume control for aeration tanks but also to the reduction of greenhouse gases. Water resources are considered to be more important in the future. HORIBA group would like to contribute to the conservation of the limited water resources through the development and sales of not only on-site water quality measuring instruments but also various kinds of automatic water quality measuring instruments.

References

- [1] I. A. Shiklomanov, J. C. Rodda, "World Water Resources at the Beginning of the Twenty-First Century", Cambridge University Press, 13 (2004)
- [2] "Water treatment-inflection dictionary first edition", Industrial Research Center of Japan, Production Goods Work Station, 71 (2012)
- [3] Hiroyuki Nagatsu, *J. EICA*, **17 (2-3)**, 31 (2012)
- [4] Takumi Ohara, PA2005199116 (JP)
- [5] Takumi Ohara, PA2003136086 (JP)
- [6] JIS K 0400 (2010), Japanese Industrial Standards Committee
- [7] JIS K 0400 (2010), Japanese Industrial Standards Committee
- [8] Akio Ishii, PP5144829(JP)



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