Development of a photometric method to measure molecular oxygen in water

Tu DANG,* † Hiroto KAWAGISHI,** Yusuke FUJII,* Kenji OKITSU,* Yasuaki MAEDA,*** Norimichi TAKENAKA*

* Graduate School of Humanities and Sustainable System Sciences, Osaka Prefecture University, Osaka 599-8531, Japan
** Graduate School of Engineering, Osaka Prefecture University, Osaka 599-8531, Japan
*** Research Organization for University-Community Collaborations, Osaka Prefecture University, Osaka 599-8531, Japan

† To whom correspondence should be addressed.
E-mail: tudt93@gmail.com

Abstract

A photometric method to determine molecular oxygen in water was developed. When manganese(II) is oxidized by oxygen under alkaline conditions, the presence of polyphosphate can prevent the precipitation due to a coacervate reaction. The oxidized manganese later dissolves in acid to form a pink Mn(III) species, which has a stable UV/vis spectrum. The monitoring of the oxygen concentration based on the absorbance of the pink Mn(III) species at 517 nm showed a strong correlation with both the Winkler method and an optical sensor. As a result, the present method can measure not only dissolved oxygen but also fine bubbles oxygen in the water sample with high reliability (0-26 mg dm$^{-3}$, $r^2 = 0.9995$). During this process, no significant interference from nitrite or metal ions was observed. The accuracy of measurement was steady at high temperatures of the water samples ($\leq 363$ K).

Key words Dissolved oxygen, ultrafine bubbles oxygen, coacervate reaction, UV/vis photometry
Introduction

Molecular oxygen is a crucial water quality parameter due to the participation of free oxygen in various chemical, biological and physiological activities.\(^1\) When oxygen molecules are diffused in water, they dissolve and remain stable under the certain equilibrium condition defined by Henry’s Law. The amount of oxygen dissolved in water is a fundamental element of a healthy aquatic environment, which is easily affected by the change of natural factors (e.g., temperature, salinity and aquatic ecosystem). Therefore, it is of practical significance to accurately monitor and evaluate the oxygen level in water.

In addition to dissolved oxygen (DO), oxygen molecules are also present in the water body in the form of suspended gas bubbles. This state of oxygen is unsteady and often neglected in the measurement because gas bubbles easily rise up and burst at the water surface.\(^2\) However, in the past decade, ultrafine bubble (UFB) oxygen, which has the bubble diameter less than 1 μm, has attracted much attention due to its unique stability in the gas-liquid phase. The decrease in gas transfer rate from bubble to liquid under the supersaturated condition enables UFBs to last from several days to a month in a water body.\(^3\) Another reason for the stability of UFBs is the electrical charged surface property, which prevents them from pulling together to form a larger bubble that might dissolve in water.\(^4\) Although the potential of UFBs has been reported in various applications of water treatment and health science,\(^2,5\) limited research has been conducted on the determination of UFBs in water.\(^6\) Thus, the behavior of UFB oxygen with different measurement approaches remains an open topic.

There are three well-known methods to measure the oxygen content in water: the Winkler chemical method, an electrochemical sensor and an optical sensor. In general, the Winkler method based on the iodometric titration technique is widely used with high reliability in laboratory environment.\(^7,8\) However, the titration process of the Winkler method is time-consuming and only suitable for discrete measurements. To date, this problem has been overcome by the application of advanced sensing technologies. The electrochemical sensor can quickly provide measurements of DO by quantifying the diffusion current generated upon the reduction of oxygen in an electrode. Despite its simplicity, the electrochemical sensor requires frequent maintenance, and its analyzing process may interfere with the oxygen content of the sample.\(^9\) The optical sensor is a stable and reliable method to monitor DO in real time. The principle is based on the quenching of oxygen to
the fluorescence signal which is highly steady and resistant to interferences. With the outstanding performance, the optical sensor is usually commercialized at high cost.

Considering the advantage and disadvantage of the current techniques, this work aims to develop a continuous system with the common equipment in the laboratory to quantify the oxygen level in water. In the Winkler method, Mn(II) is easily oxidized in alkaline medium, but the employment of iodine requires a labor-intensive titration process. In the attempt to directly measure the amount of oxidized manganese, we utilized the coacervate reaction of high polymerized compound to prevent the precipitation of manganese in the solution. Interestingly, by introducing polyphosphate to an alkaline solution, we have found that not only the precipitation process is prevented, but after the acidification step, a stable coacervated manganese(III) species forms, which has a specific UV/vis spectrum. Based on the formation of the coacervated manganese(III) species, it is possible to develop a flow system to measure DO in water. All setting conditions were optimized to shorten the analyzing time and increase the Mn(III) formation. Finally, we evaluated the interference of some common species and demonstrated the accuracy of the method in measuring real water sample.

Experimental

Chemicals and reagent.

All chemicals were of analytical grade and obtained from Wako Pure Chemicals Industry Ltd. The solution was prepared using ultrapure water produced by a Direct-QR 3 UV water system (Millipore SAS, 67120) with resistivity above 18.2 MΩ cm. Nitrogen (99.99995%) and oxygen (99.5%) cylinder gases were supplied from Taiyo Nippon Sanso Co. Ltd.

The water sample used for analysis was tap water in Osaka Prefecture University. The water quality followed National Effluent Standards of Japan. Before the experiment, the water sample was overflowed into a 2-liter cylinder-shape vessel (approximately 25 cm long and 10 cm in diameter) with a valve near the bottom for sampling purpose. The sampling and monitoring spots were designed near the bottom area for the stable oxygen value during the experiment.

UFB O₂ was generated by a gas-water circulation generator from Nano-Science Laboratory Corporation (Japan). The oxygen concentration in water was controlled by changing the concentration of gaseous oxygen in nitrogen/oxygen mixture gas sources. Although the
supersaturated condition of oxygen remained stable over 3 days, the water samples were daily prepared.

**Equipment**

DO and UFB oxygen in water were continuously monitored by the Hach, HQ30D optical sensor with a measurement range of 0.01-20.00 mg dm$^{-3}$. At oxygen concentrations above 20 mg dm$^{-3}$, only the Winkler method was utilized as the reference. The sample and reagents were carried into the system by a Tokyo Rikakiki Co. Ltd., MP-2000 peristaltic pump and a Reglo Analog, 796-B multichannel Ismatec pump, respectively. The flow rates of the pumps were checked weekly for stabilizing purpose. The manganese(III) solution was measured by a Shimadzu Co. Ltd., model 1800 UV/vis spectrophotometer. Nikon polarizing microscope (ESCLIPE LV100) and 50X magnification lens (CFI TU Plan Flour EPI) were used to investigate the coacervation formation.

In the UFB oxygen monitoring, the electrochemical sensor (LUTRON 5509, range of 0.1-20.0 mg dm$^{-3}$) and the Winkler method were used in parallel as the reference. The electrochemical sensor was calibrated 30 minutes before every experiment. In the Winkler method, each 100-cm$^3$ sample was carefully taken out from the valve near the vessel bottom to a BOD bottle for triplicate measurements. The Winkler procedure followed the Testing methods for industrial wastewater Japan (JIS K0102).

A silicone tube with an inner diameter of 0.15 mm was used to carry the sample/reagent. Two mixing coils (10 loops of silicone tube) were set up outside the water bath to achieve the complete mixing. The PTFE tube with an inner diameter of 0.20 mm and an outer diameter of 0.25 mm was used for ultrasonic irradiation inside the water bath. A mixing coil (2 loops of this PTFE tube) was made to prolong the reaction time. The PTFE coil was placed near the transducer area, so the cavitation pressure from the standing wave could prevent manganese from sticking on the inner tube. It was critical to adjust the coil below the water surface to match the antinode position, where the maximum acoustic pressure occurred.

An AS ONE Co. Ltd. US-2 type ultrasonic automatic washer (frequency of 38 kHz) with a temperature control feature was utilized. During the measurement, a circulation pump was implemented to maintain the bath temperature at 288K.

**Interference study**
All samples were collected into BOD bottles followed the Winkler procedure. Then, 0.5 cm$^3$ solution of interference species was added to the bottle sample. The mixture was stirred for 30 minutes by a magnetic stirrer (AS ONE, REXIM RSH-1DN). In this process, the bottle was capped to prevent the change in oxygen content.

The oxygen concentration in high-temperature water was investigated using the heated water bath (AS ONE Co. Ltd., EW-100R). Three liters of tap water were poured into the bath and heated for 30 minutes in the temperature range of 303-363 K. The water temperature was continuously controlled by a temperature controller. Due to the temperature limitation of the electrochemical sensor and optical sensor, only the Winkler method was used as the reference.

**Measurement of real samples**

Nine samples of surface water (lake and drainage) and rainwater were tested in triplicate by both photometric method and optical sensor (Hach, HQ30D). Before each measurement, the turbidity of the sample was calibrated by the autozero function.

**Results and discussion**

**Mechanism of Mn(III) formation**

In preliminary experiments using a biochemical oxygen demand bottle, Mn(II) is oxidized in the alkaline medium to form a brown precipitate of Mn(IV). After few minutes, the precipitate gradually sinks to the bottom, as shown in Fig. 1A as the floc of insoluble oxides. Afterward, the addition of (NaPO$_3$)$_6$ and H$_2$SO$_4$ to the precipitate solution slowly created a bright pink Mn(III) coacervation. The progressively transformation of manganese spectrum recorded by UV/vis spectroscopy showed that Mn(IV) is gradually reduced to Mn(III), which has a spectrum with a wide absorbance peak around 517nm. (Fig. S1)

By adding hexa-metaphosphate before precipitating manganese (reactions 1 and 2), we accelerated the formation rate of Mn(III) species (within 2 minutes) due to an early coacervation reaction. This is 50 times faster compared to the 60 minutes of formation rate that shown in Fig. S1.

$$[O_2 + \text{OH}^- + (\text{NaPO}_3)_6] + \text{Mn}^{2+} \rightarrow \text{Mn(IV)} \quad (1)$$
\[
\text{Mn(IV)} + \text{H}^+ \rightarrow \text{Mn(III)}_{\text{coacervation}} \quad (2)
\]

In the presence of polyphosphate, the oxidized reaction creates a brown mixture that remains in suspension for a long time due to the viscous coacervate phase, which is immiscible in water.\(^{14}\) In this phase, both coacervate process and oxidized process appear to simultaneously occur as shown in Fig. 1B as many white coacervate droplets and black oxidized manganese particles interspersed among one another.

By using high concentration of polyphosphate solution in reaction (1), only a white block of coacervation was observed to be formed. As shown in Fig. 1C, the coacervate sedimentation was made of many white small coacervation, which is also called the “hardening phenomenon”, where the coacervate is sufficiently dense to deposit.\(^{15}\) This coacervation block sinks to the bottom, and the water solution remains clear, which indicates that no redox reaction occurs and the coacervate reaction will be favored by an increase in polyphosphate concentration. The dissolution of the coacervation block in acid does not form a pink Mn(III) species, so the coacervate compound is Mn(II). Hence, the brown color of the mixture obviously comes from the oxidized manganese as the Mn(IV) species.

After acidification, the mixture solution containing Mn(II)\(_{\text{coacervation}}\) and Mn(IV) quickly transforms to the pink Mn(III) species. This Mn(III) solution is stable at room temperature for more than 3 weeks before slowly degrading. Unlike the easily disproportion of Mn(III), a steady-state condition of this Mn(III) species suggests that its colloid is also protected by polyphosphate. Regarding the similarities of the Mn(III) species found in this work and the trivalent manganese coacervate of the previous report,\(^{16}\) the term “Mn(III)\(_{\text{coacervation}}\)” was utilized. A proposed reaction mechanism is presented as follows:

\[\begin{align*}
\text{O}_2 + (\text{NaPO}_3)_6 + \text{Mn(II)} \xrightarrow{\text{OH}^-} & \quad \text{Mn(II)\(_{\text{coacervation}}\) + Mn(IV)} \xrightarrow{\text{H}^+} \text{Mn(III)\(_{\text{coacervation}}\)} \\
\text{Oxidized by } \text{O}_2 \\
\text{Protected by polyphosphate (priority reaction)}
\end{align*}\]
In this reaction pathway, a part of Mn(II) will be oxidized to form Mn(IV), while the other part will form Mn(II)\textsubscript{coacervation}. Since the role of polyphosphate is to stabilize metal colloid particles, the increasing polyphosphate content will create Mn(II)\textsubscript{coacervation} in priority and slow down the formation of Mn(IV). In the presence of sulfuric acid, Mn(II)\textsubscript{coacervation} reacts with Mn(IV) to form Mn(III)\textsubscript{coacervation}.

Based on the proposed mechanism, the photometric system was developed to continuously monitor the oxygen concentration (Fig. 2). The measurement procedure in the system was described as follows:

1) The water sample [9 cm\textsuperscript{3}/min] was mixed with NaOH [0.5 cm\textsuperscript{3}/min] and (NaPO\textsubscript{3})\textsubscript{6} [0.5 cm\textsuperscript{3}/min].
2) Next, the mixture reacted with [0.5 cm\textsuperscript{3}/min] Mn(II) inside a reaction coil to form Mn(IV). An ultrasonic bath was operated to enhance the mixing efficiency.
3) Finally, the mixture solution was dissolved by H\textsubscript{2}SO\textsubscript{4} [1 cm\textsuperscript{3}/min] to form the pink Mn(III)\textsubscript{coacervation}, which was monitored by UV/vis spectroscopy at 517 nm wavelength.

**Optimum condition of reagents concentration**

The effect of reagent concentrations on the formation of Mn(III) species were examined. Figs. S2 A and B show a similar pattern of Mn(III) absorbance related to the change of Mn(II) and NaOH, respectively. The Mn(III) absorbance sharply increases with increasing Mn(II) and NaOH concentrations and reaches the highest peak before slowly declining when the amounts of both reagents become excessive. Since the amount of NaOH should be excessive to completely oxidize manganese in the solution, 1.5 mol dm\textsuperscript{-3} Mn(II) and 5 mol dm\textsuperscript{-3} NaOH are selected as the optimized condition.

The coacervation process strongly depends on the proportion of polyphosphate/metal colloid.\textsuperscript{17} The relationship of Mn(III) – polyphosphate shown in Fig. S2C is consistent with our proposed mechanism. The increase in polyphosphate concentration will generate more Mn(III) species till the optimized state. Beyond this point, further addition of polyphosphate creates more Mn(II)\textsubscript{coacervate} and reduces Mn(IV), which decreases the Mn(III) formation. Considering the role of polyphosphate to stabilize manganese colloid and prevent flocculation, 0.2 kg dm\textsuperscript{-3} of polyphosphate is selected.
The higher concentration of H\(_2\)SO\(_4\) could accelerate the dissolution of Mn(IV) to form Mn(III). Fig. S2D shows that the Mn(III) absorbance is maximized at 1 mol dm\(^{-3}\) H\(_2\)SO\(_4\) and subsequently declines with increasing acidity. We presume that the cause for the degradation is the competition of H\(^+\) ion with Mn(II) ion in the polyphosphate interaction. Since the role of acidity in this reaction requires further investigation, thus, 1.4 mol dm\(^{-3}\) of H\(_2\)SO\(_4\) is selected to eliminate the risk of indissoluble Mn(IV). All optimal conditions for further research are summarized in Table 1, the optimized condition of flowrate and bath temperature can be found in Supporting information section.

**Measurement of DO and UFBs oxygen.**

The results from two separate studies at oxygen ranges of 0.4 – 10 mg dm\(^{-3}\) and 10 – 20 mg dm\(^{-3}\) show an almost perfectly linear relationship \((r^2=0.9996)\) between the photometric method and the optical sensor (Fig. 3). All tests shown in Fig. 3 have relative standard deviations below 2\%, which indicates the high reliability of the proposed method.

The oxygen concentration was comparatively measured by an electrochemical sensor and the Winkler method. Although there were no significant differences among four methods in measuring DO, the sensing capability of the electrochemical sensor was weaker in the measurement of UFB oxygen (Fig. 4) despite continuous stirring. There may be three main reasons that cause the underperformance of the electrochemical sensor: (1) the size of UFB oxygen makes it difficult to pass through the polymeric membrane, which results in less oxygen being reduced at the cathode;\(^{6,9}\) (2) the negative charge of UFB oxygen possibly reduces its ability to give away electron; (3) the reaction rate at the cathode greatly depends on the gas mass transfer, which is reduced under the supersaturated condition.\(^{3}\) Meanwhile, the other three methods provide similar results, which suggests that the oxygen-quenching process and chemical reaction were not affected by the existing UFBs. Consequently, the measured oxygen concentrations were highly matched with the titrated results of the Winkler method, which was presented as the linear regression line in Fig. 4 (0.4-26 mg dm\(^{-3}\), slope = 0.9889, \(r^2=0.9995\)). Above this oxygen concentration, the photometric method provided lower values than those of the Winkler method, even a strong correlation of the fitting model was obtained in the whole range of oxygen level (0.4-39 mg dm\(^{-3}\), slope = 0.9166, \(r^2=0.996, N=29\)). It is due to the insufficient reaction rate of the current sample flow speed, which can be improved by increasing the pumping velocity.
**Effect of interference**

In the selectivity test, five sources of metal ions were separately introduced into the system to find the maximum tolerable concentration of each species. The results in Table 2 show the strong resistance of this method to some common metal ions that often disturb the titration process (e.g., ferrous iron, manganese). All tested concentrations of foreign substances were much higher than allowed by water quality standard,\(^{11}\) so no significant interference was found.

Nitrite is well known as an unpleasant ion that seriously interferes with the Winkler method even in the micromolar concentration range. Although nitrite is slowly oxidized to nitrate at normal water temperature,\(^{18}\) it quickly oxidizes iodide to iodine molecule in the acidification step of the Winkler test, and the cycle reaction may continue if free oxygen is available.\(^{7}\) Thus, the addition of sodium azide must be required to eliminate nitrite before the analysis. In the proposed method, free of iodine, the measurement process was dependable up to \(3.5 \text{ mg dm}^{-3}\) of \(\text{NaNO}_2\). Compared to the acceptable threshold of nitrite (13.8 \(\mu\text{g dm}^{-3}\)) for the Winkler method in previous report,\(^7\) this approach has removed the concern about an overestimation of DO caused by nitrite interference. Since the natural water generally contains much less than 2 \(\text{mg dm}^{-3}\) of nitrite,\(^{19}\) the effect of nitrite is also negligible.

**Effect of the sample temperature**

In many measurement situations, the sample temperature is a serious limitation to the current sensors. Although many advanced sensors acquire a temperature compensation module to correct the oxygen value, they normally operate up to 323 K. By examining the performance of the photometric method under high temperature conditions (303-363 K), we found that the measurement process was steady through all temperature ranges (compared to the Winkler method). Furthermore, the obtained results (Fig. 5) are consistent with other findings of oxygen solubility as a function of temperature.\(^{20,21}\) Because the increasing temperature only accelerates the chemical reaction rate in this closed system, the proposed method is efficient for detecting oxygen levels at high solution temperature.

**Measurement of real samples**
As shown in Fig. 6, an excellent correlation obtained by the photometric and optical method suggests that the photometric method is applicable for different water samples (slope=1.0009, \( r^2 = 0.9993 \)). Although the baseline calibration of each sample was applied before the measurement process, to completely prevent the light scattering effect of turbidity in the UV/vis measurement, all pumps were stopped before recording the result. Since no suspended particles entered the quartz cell, subsequently, all measured results (Table S1) displayed a small relative standard deviation (less than 3.2%), which demonstrates the stability of the proposed method even for turbid samples. In summary, the proposed method can rapidly quantify the DO level in natural water samples with similar accuracy to an optical sensor.

**Conclusions**

In this work, we present the development of a photometric method to measure molecular oxygen in water. Based on the polyphosphate coacervated reaction, the concentration of both DO and UFB oxygen was quickly evaluated regarding to the absorbance spectrum of Mn(III) species. This method offers a wider linearity detection range (26 mg dm\(^{-3}\)) than the optical sensor and higher sensitivity than the electrochemical sensor in measuring samples containing UFB oxygen. In addition, the sensitivity study observed no significant impact from nitrite, metal ions and even high temperature. Thus, the DO levels in different natural water samples were measured with reliability. Considering this finding, future studies will strive for more detail about the reaction mechanism and determination of molecular oxygen in seawater.
Acknowledgements

The author would like to acknowledge the valuable assistance and support of the Graduate Course for System-inspired Leaders in Material Science (SiMS) Program in Osaka Prefecture University.
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Table

Table 1. Optimized condition of the flowrate and concentration in the photometric system

* Unit is kg dm\(^{-3}\)

| Variable         | Flowrate (cm\(^3\) min\(^{-1}\)) | Concentration (mol dm\(^{-3}\)) |
|------------------|----------------------------------|---------------------------------|
| Water sample     | 9                                | -                               |
| NaOH             | 0.5                              | 5                               |
| (NaPO\(_4\))\(_2\) | 0.5                              | 0.2*                            |
| Mn(II)           | 0.5                              | 1.5                             |
| H\(_2\)SO\(_4\)  | 1                                | 1.4                             |
| Ultrasonic bath temperature | 288 K                           |                                  |

Table 2. Interference study in the optimized condition of the photometric system

| Interference substances | Concentration (mg dm\(^{-3}\)) | Relative Error (%) |
|-------------------------|---------------------------------|--------------------|
| Zn(II)                  | 100                             | -3.9               |
| Cu(II)                  | 100                             | -0.3               |
| Mn(II)                  | 50                              | 4.7                |
| Fe(II)                  | 15                              | 5.5                |
| Cr(III)                 | 20                              | 5.9                |
| Nitrite                 | 3.5                             | -5.2               |
Figure Caption

Fig. 1 Microscopy images of solution contained (A) manganese(IV) precipitation (NaOH 5 mol dm\(^{-3}\), Mn(II) 1.5 mol dm\(^{-3}\)); (B) coacervated manganese(II) as white droplets and oxidized manganese(IV) as black particles (NaOH 5 mol dm\(^{-3}\), (NaPO\(_3\))\(_6\) 0.2 kg dm\(^{-3}\), Mn(II) 1.5 mol dm\(^{-3}\)); (C) coacervated manganese(II) (NaOH 5 mol dm\(^{-3}\), (NaPO\(_3\))\(_6\) 2 kg dm\(^{-3}\), Mn(II) 1.5 mol dm\(^{-3}\)).

Fig. 2 Schematic diagram of the oxygen measurement system.

Fig. 3 Correlation of the present photometric method (NaOH: 5 mol dm\(^{-3}\); (NaPO\(_3\))\(_6\): 0.2 kg dm\(^{-3}\); Mn(II): 1.5 mol dm\(^{-3}\); H\(_2\)SO\(_4\): 1.4 mol dm\(^{-3}\); flowrate: 9 cm\(^3\)/min; 288 K bath temperature, 100% O\(_2\) saturated condition) with the optical sensor at different oxygen concentrations.

Fig. 4 Comparative measurement at different oxygen concentrations. **Circle**: photometric method (NaOH: 5 mol dm\(^{-3}\); (NaPO\(_3\))\(_6\): 0.2 kg dm\(^{-3}\); Mn(II): 1.5 mol dm\(^{-3}\); H\(_2\)SO\(_4\): 1.4 mol dm\(^{-3}\); 100% O\(_2\) saturated condition); **Square**: Optical sensor; **Triangle**: Electrochemical sensor. A calibration line of photometric method is generated based on oxygen concentrations up to 26 mg dm\(^{-3}\).

Fig. 5 Solubility of oxygen in water at different temperatures. **Square**: Winkler method; **Circle**: photometric method; **Triangle**: Distilled water - Mel’nichenko study (2008);**Cross**: Pure water - Geng study (2010).

Fig. 6 DO measurement of real samples. **Triangle**: Drainage water; **Circle**: Lake water; **Square**: Rainwater.
Fig. 1
Fig. 2
Fig. 3

\[
y = 0.0076x + 0.0246 \\
R^2 = 0.9996
\]
Fig. 4

\[ y = 0.9889x - 0.0439 \]

\[ R^2 = 0.9995 \]
Fig. 5
Fig. 6