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Optimization of Chemical Oxygen Demand Determination in Seawater Samples Using the Alkaline Potassium Permanganate Method

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Abstract – Chemical oxygen demand (COD) is a practical parameter that is used to estimate the amount of organic pollutants in aqueous systems. It is generally used as a guideline to control the quality of waste treatment effluent globally and is a management tool to evaluate the total pollution load in the highly developed coastal regions of Korea. It is a preferred method because of the speed and simplicity of the analysis and because there are fewer instrumentation requirements. The Ministry of Oceans and Fisheries (MOF) of the Republic of Korea developed a standard procedure for the measurement of COD. It has been revised several times, and the most recent revision was made in 2013 (MOF 2013-230). In this study, we modified the standard COD measurement procedure (MOF 2013-230), especially the sample digestion apparatus, to enhance analytical efficiency for a large sample number (batch), which is called a Korea Institute of Ocean Science and Technology (KIOST) modified MOF 2013-230. We examined uncertainty related to each experimental step and optimized laboratory conditions to reduce such uncertainties. The detection limit and estimated expanded uncertainty related to the KIOST modified MOF 2013-230 was 0.18 and 0.11 mg O_2/L at a 95% confidence level ($k = 2$), respectively. This study also provides several tips to maintain consistent COD measurements in seawater using the alkaline potassium permanganate method.

Keywords – chemical oxygen demand, KIOST modified MOF 2013-230, COD detection limit, COD uncertainty, alkaline potassium permanganate method

1. Introduction

The content of organic pollution in aqueous systems is assessed by the chemical oxygen demand (COD), biological oxygen demand (BOD), and total organic carbon (TOC). COD is a measure of the nonspecific organic matter content in samples; it measures the oxygen requirement during the decomposition of organic matter and oxidation of inorganic chemicals such as ammonia and nitrite. COD has an advantage over BOD and TOC for monitoring pollution due to the speed and simplicity of the analysis and fewer equipment requirements, respectively. Thus, COD is a very effective method for determining organic pollution in aqueous systems and is used as a practical indicator of the organic matter concentration and water quality (Kawabe and Kawabe 1997; Kim et al. 2001). In the European Commission Urban Waste Water Treatment Directive 91/271/EEC, COD is the primary method used to monitor wastewater before (influent) and after (effluent) treatment to protect the environment and ensure the economic sustainability of the treatment facility. In Korea, it is a key parameter for total pollution load management (TPLM) of highly polluted coastal regions (Chang et al. 2012).

The potassium dichromate method is commonly used for COD measurements of waste water and highly polluted surface waters due to its superior oxidizing power, good reproducibility, and facile handling (Tsonis 1993). However, the potassium dichromate method under acidic conditions is severely influenced by chloride ions in the sample so it cannot be applied to saline water. Instead, the potassium permanganate method under alkaline conditions is commonly employed for COD determination in unpolluted highly saline water (Baumann 1974; Nihonkikaku 1993).

The standard procedure for marine environment COD

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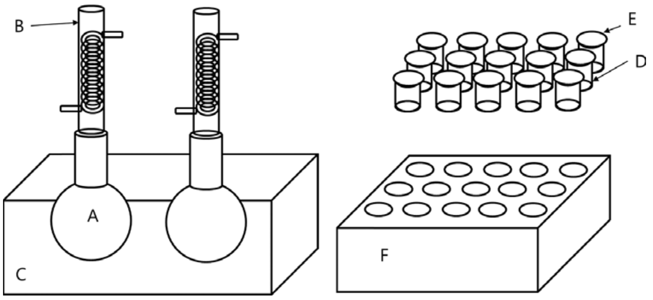

Fig. 1. Schematic diagram of COD reaction vessels of the MOF2013-203 (left) and KIOST modified MOF2013-203 (right) method: A, 250-mL round bottom flasks; B, graham condenser; C, water bath (100°C); D, 100-mL borosilicate beaker without spout; E, borosilicate watch glass; and F, water bath (100°C)

measurements adopted in Korea is the potassium permanganate method with an open reflux under alkaline conditions and has been revised several times. In the MOF 2013-230 revision, sample digestion was conducted using a 250-mL Erlenmeyer flask with a condenser. Although there was no specific description of how the condenser was attached to the reaction vessel, a graham condenser was generally used in commercially available reaction vessels (Fig. 1). Maintenance of reaction vessels with a graham condenser is very tricky - making it very hard to use more than 10 reaction vessels in each experiment. Thus, extra effort was required to process several hundred samples within a short period and required the use of many laboratories and environmental analytical services. There was also no specific statement on the precision and detection limit in the MOF 2013-230 revision, which restricts the use of COD as a guideline for TPLM.

In this study, we modified the reaction vessels to enhance their analytical efficiency and evaluated the uncertainty related to each procedure in the experiment. We also recommend some procedures to maintain a high-quality COD analysis.

2. Materials and Methods

Analytical method

In the standard procedure MOF 2013-203, seawater samples (25–50 mL) for the COD analysis were transferred to 250-mL Erlenmeyer flasks and treated with 1 mL of 20% (w/v) NaOH followed by 10 mL of 0.025 N $KMnO_4$ (Fig. 1). Then, the flask with a condenser was placed in a boiling water bath for 60 min. The sample in the flask should be lower than the water line of the bath. After the reaction, the condenser was cleaned with a small amount of deionized water (DIW) and removed from the flask. Then, the flask was cooled down to room temperature and 1 mL of 10% (w/v) KI and 5 mL of 10% (v/v) H_2SO_4 were added to the flask.

The amount of $KMnO_4$ that remained in the reaction vessels was directly measured using 0.025 N$Na_2S_2O_3$ to estimate the amount of $KMnO_4$ that was used for the reaction. A Schott Titronic Universal Titrator with a 50-mL syringe or a Metrohm Titrator with 20-mL syringe was used. For the titration, 0.025 N $Na_2S_2O_3$ solution was continuously transferred to the reaction vessels until the orange color had almost disappeared, 1 mL of a 1% (w/v) starch solution was then added into the reaction vessels, which turned the sample purple. The titration continued until the purple color disappeared. The COD concentration was calculated by the following equation:

$$\text{COD (mg } O_2\text{/L)} = [(V_{Na_2S_2O_3blank} - V_{Na_2S_2O_3sample}) \times C_{Na_2S_2O_3} \times 8/V_{sample}\,(\text{mL})] \times 1000 \quad (1)$$

where $V_{Na_2S_2O_3blank}$ is the volume of $Na_2S_2O_3$ used in the titration of blank, $V_{Na_2S_2O_3sample}$ is the volume of $Na_2S_2O_3$ used in the titration of the sample, $V_{Na_2S_2O_3}$ is the normal concentration of $Na_2S_2O_3$, and V_{sample} is the amount of sample used to measure the COD concentration (mL). The factor 1000 is used to convert the COD concentration unit from mL to L. To calculate the COD concentration, at least triplicates of blank concentration using DIW have to be measured.

Reagent preparation

We carefully followed the instructions in MOF 2013-230 to prepare the reagents. Especially, we paid great attention to the preparation of 0.025 N $KMnO_4$, 0.025 N $Na_2S_2O_3$, and the 1% starch solution. We dried powder reagents before weighing and recorded the temperature and humidity of the laboratory, which were used for the buoyancy correction. All reagent solutions were discarded after 1 week and were made fresh for the next measurement.

Natural samples for long-term COD measurements

Natural seawater samples for long-term COD measurements using the Korea Institute of Ocean Science and Technology (KIOST) modified MOF 2013-230 were prepared by Rho et al. (2015). Seawater samples were taken from the coastal region and pre-filtered through a 0.2-mm membrane filter (STyLUX, MEISSNER). The COD concentration of pre-filtered seawater was about 6.0 mg O_2/L, which was diluted to around 2.0 mg O_2/L with surface seawater taken from the Ulleung Basin of the East Sea. The sample was transferred to a titanium container, sterilized at 210 kPa at 120°C for 2 h, cooled down to room temperature, homogenizing by rotation of the container, and then transferred to a 500-mL narrow mouth Nalgene HDPE bottle in a Class 100 clean bench. Sample bottles were sealed with an aluminum film airtight bag and stored at room temperature.

3. Results and Discussion

Modification of the reaction vessel configuration

In this study, we modified the reaction vessels from a 250-mL Erlenmeyer flask with a condenser to a 100-mL borosilicate glass beaker without a spout (Duran, Germany) and a borosilicate watch glass with a fused edge cover to protect from foreign material input and air condensation during the sample digestion process; this is called the KIOST modified MOF 2013-203 method (Fig. 1). For the reaction water bath, we used a general-purpose water bath to make the reaction of 15 samples simultaneously, which can be extended to as many as 50 samples by using a customized water bath. According to the matched-pair *t*-test, the comparison of two methods showed no apparent difference at the 95% confidence level (Table 1). Therefore, the KIOST modified MOF 2013-203 method can be used as an alternative COD reaction method to MOF 2013-230. The KIOST modified MOF 2013-203 method has the great advantage of being able to measure a large number of samples simultaneously (up to ~50 samples including a blank sample) compared with the MOF 2013-230 method using a 250-mL Erlenmeyer flask with a graham condenser.

Identification of uncertainties

Several factors may affect the accuracy and precision of the COD measurement as follows.

1) The accuracy and precision of the sample volume used plays an important role in the COD concentration calculation.

2) The reaction conditions, such as contamination of the reaction vessels used and homogeneity of the water temperature in the water bath, may influence the accuracy of the COD measurement.

3) Accurate assessments of the added $KMnO_4$ and $KMnO_4$ used for the reaction are the most important factors that can affect the accuracy of COD measurements in a sample. This is because the amount of COD in samples was calculated by the difference in $KMnO_4$ added to the sample and $KMnO_4$ used in the sample during the reaction. The accuracy in determining the amount of $KMnO_4$ used is partly related to the reaction conditions and accuracy of the endpoint determination that is highly dependent on personal experience and the volumetric resolution of the instrument used in the titration. Thus, we estimated the uncertainty related to the endpoint determination.

4) The amount of $KMnO_4$ added to the reaction vessel is also important in controlling the accuracy and precision of COD measurement. We estimated uncertainty caused by the pipetting of $KMnO_4$ into the reaction vessels.

5) The total amount of $KMnO_4$ used for the reaction is related to reaction capacity, which may affect the COD measurement result. This is because, from time to time, the concentration of $KMnO_4$ is modified to 0.01 N to correspond to 0.01 N $Na_2S_2O_3$, which was frequently adjusted to reduce the error related to the endpoint determination.

6) The influence of reaction time on COD determination is also evaluated.

7) We estimated the influence of other nitrogen compounds,

Table 1. Comparison of the reaction method between the MOF 2013-203 open reflux method and the KIOST modified method. The reaction vessel and condenser configuration are different but the reagents and other conditions are the same for both methods

Tests	MOF 2013-203 open reflex (A)	KIOST modified open reflex (B)	Differences (A - B)
	COD (mg/L)	COD (mg/L)	
Test 1	5.68	5.69	-0.01
Test 2	5.72	5.64	0.08
Test 3	5.60	6.09	-0.49
Test 4	5.60	5.74	-0.14
Test 5	5.20	5.57	-0.37
Test 6	4.88	5.73	-0.85
Test 7	3.76	3.61	0.15
Test 8	3.76	3.50	0.26
Mean			-0.17 ± 0.37

such as nitrite, nitrate, and ammonia, in the sample for the determination of COD concentration.

8) We also evaluated the consistency of reagent preparation for the COD determination.

9) The accuracy and precision of $Na_2S_2O_3$ are also important factors for uncertainty in COD determination.

Uncertainty related to the sample volume

Samples (50 mL) were transferred into the reaction vessels with a 10-mL electronic pipette (RAININ E4 XLS) that has an accuracy of ± 60 μL for 10-mL transfers. There are several elements that may affect the accuracy and precision in volume transfer using a pipette, such as the temperature of a laboratory, angle and immersion depth, and personal experience. To reduce the uncertainty in sample volume transfer by laboratory temperature, we maintained a constant room temperature of 25 ± 2°C. The electronic pipette was fixed perpendicular to the sample container, and we tried to take the sample from the same depth. Under the condition described above, the measured accuracy of volume transfer using the 10-mL pipette was ± 9 μL ($n = 10$) in a 10-mL transfer and five 10-mL sample transfers were made. So, the standard deviation for a sample transfer is ± 45 μL. This results in a change of ± 0.00004 mg O_2/L, an effect that seems to be insignificant.

Uncertainty related to the reaction conditions, including the laboratory environment

The uncertainty of the reaction conditions is related to the cleanness of reaction vessels and the homogeneity of reaction temperature within the water bath, including the other uncertainties mentioned previously. The uncertainty of the reaction conditions was estimated using DIW as a blank sample. Using a 10-mL electronic pipette, 50-mL DIW and 10-mL $KMnO_4$ solutions were transferred into 10 reaction vessels, which were evenly placed in the boiling water bath for 60 min. COD determination was conducted in the same as described in the method section. The standard deviation of the 0.025 N $Na_2S_2O_3$ volume used in the titration of 10 blank samples was ±14 μL, which corresponds to ± 0.057 mg O_2/L. The standard uncertainty related to the reaction conditions was calculated as $0.057/\sqrt{10} = 0.0163$ mg O_2/L, which included all of the combined uncertainties related to the sample and $KMnO_4$ transfers into the reaction vessels, homogeneities of reaction vessels, reaction temperature within the water bath, and the uncertainty related to the detection of the endpoint, such as personal experience and instrument resolution.

Uncertainty related to detection of the endpoint

Two factors influenced the precision of endpoint detection: the increment volume of the titrant and detection of the endpoint. The instruments used to titrate the remaining $KMnO_4$ after the reaction (estimation of $KMnO_4$ used during the reaction) using 0.025 N $Na_2S_2O_3$ were a Schott Titronic Universal Titrator with a 50-mL syringe (an increment volume of 0.01 mL) or a Metrohm Titrator with a 20-mL syringe (0.002 mL increment volume). On the basis of the repeated experiments, at least 8–10 mL of 0.025 N $Na_2S_2O_3$ was required to identify the color change from purple to transparent. This equates to at least 0.032–0.040 mg O_2/L. Personal experience is very critical for detection of the endpoint. Practice is required for consistent endpoint detection within the least amount of titration solution. The stability of a 1% starch solution is also an important factor for endpoint detection consistency. A detailed description of the preparation and storage of a 1% starch solution is provided in the MOF 2013-203 method.

Uncertainty related to the $KMnO_4$ volume transfer

For the calculation of COD concentration using equation (1), the variability in the amount of $KMnO_4$ solution added to samples could be directly related to a fluctuation of the $Na_2S_2O_3$ volume during the titration ($KMnO_4$ is used during the reaction), which may be a major source of uncertainty in the COD measurement. We estimated the uncertainty of volume transfer inherent in pipetting 10 mL of 0.025 N $KMnO_4$ into the reaction vessel with the same electronic pipette under constant laboratory conditions.

The measured uncertainty was ± 9 μL in a 10-mL transfer, which results in a ± 0.036 mg O_2/L change in the calculation of COD concentration. The magnitude of uncertainty related to the transfer of 10-mL $KMnO_4$ was about 1000 times larger than that of the sample volume transfer. More attention should be paid to the transfer of the $KMnO_4$ solution into samples.

Uncertainty related to the total amount of $KMnO_4$ added for the sample reactions

There is a description in the standard procedure MOF 2013-203 that the amount of $KMnO_4$ added to the reaction vessel constrained the detection range of COD in seawater samples. It is recommended that the residual $KMnO_4$ should be greater than half of the total $KMnO_4$ added after the reaction. However, some laboratories modified the amount of $KMnO_4$ added by changing the concentration or volume of the $KMnO_4$ reagent used for the reaction. In this study, we

Table 2. Comparison of COD reaction efficiency (mg O_2/L) by the amount of $KMnO_4$ used in the reaction. The same volume (10 mL) of different $KMnO_4$ concentrations was used for the test

Samples	0.01 N $KMnO_4$	0.025 N $KMnO_4$	Difference
1	1.95	2.30	0.35
2	2.22	2.47	0.25
3	2.18	2.46	0.28
4	2.19	2.46	0.27
5	2.01	2.30	0.29
6	2.05	2.36	0.31
7	2.02	2.36	0.35
8	2.01	2.42	0.41
Mean ± s.d.	2.08 ± 0.12	2.39 ± 0.07	0.31 ± 0.05

investigated the effect of the amount of $KMnO_4$ reagent on reaction efficiency by changing the concentration of the $KMnO_4$ reagent (Table 2). For this experiment, we divided the same sample into two fractions that were treated with different $KMnO_4$ concentrations (0.01 vs. 0.025 N $KMnO_4$) with the same volume (10-mL $KMnO_4$ in a 50-mL sample). The results indicated that the reaction efficiency was about 13% higher with the 0.025 N $KMnO_4$ addition than with the 0.01 N $KMnO_4$ addition. The mean difference between the two treatments was 0.35 mg O_2/L. This result suggests that a lower $KMnO_4$ addition by changing $KMnO_4$ concentration from 0.01 N $KMnO_4$ to 0.025 N $KMnO_4$ may result in about a 13% underestimation.

The MOF 2013-203 method recommended to use a 10-mL 0.025 N $KMnO_4$ solution for a 25- to 50-mL seawater sample. It also recommended to use a 50-mL seawater sample when COD was < 8 mg O_2/L in the seawater sample. The optimal $KMnO_4$ volume was examined for a seawater sample with a COD concentration around 2.40 mg O_2/L by varying 2.5–20 mL of the 0.025 N $KMnO_4$ solution in the reaction vessels. The results suggest that COD concentration from the same samples showed an increasing trend in the range of 2.5–10 mL addition and maintained a similar concentration in the range of 10–20 mL addition (Fig. 2). Therefore, it is highly recommended to add 10 mL of 0.025 N $KMnO_4$ in a 50-mL seawater sample for a consistent COD analysis when the COD concentration is < 8 mg O_2/L.

Uncertainty related to the reaction time on the COD concentration measurement

There have been various reaction times for the measurement of COD concentration in the related literature (60 min for the MOF 2013-230 method, 120 min for the APHA (2017)). To examine the effects of different reaction times on the measurement of COD concentration, we varied the reaction time from 30 to 180 min with a 30-min interval. A higher COD concentration was measured with a longer reaction time (Fig. 3). The COD concentration with a 30-min reaction time was 12.0% lower than that with a 60-min reaction time in MOF 2013-203. However, the MOF 2013-203 recommended reaction time (60-min reaction time) may underestimate the COD concentration by about 6.0%, 10.3%, 11.1%, and 14.5% compared with the 90-, 120-, 150-, and 180-min reaction time, respectively. In this study, we used the 60-min reaction time to maintain consistency with previous measurements using MOF 2013-203.

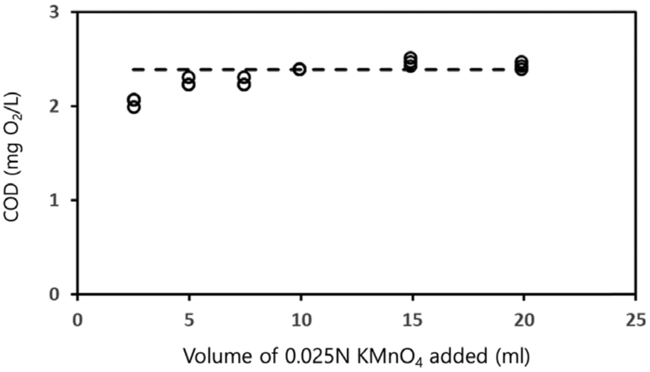

Fig. 2. Effect of $KMnO_4$ amount added to reaction vessels. Different volumes (2.5, 5.0, 7.5, 10.0, 15.0, and 20.0 mL) of 0.025 N $KMnO_4$ solution was added to reaction vessels to estimate the effect of total amount of $KMnO_4$ on the reaction of organic materials in the sample

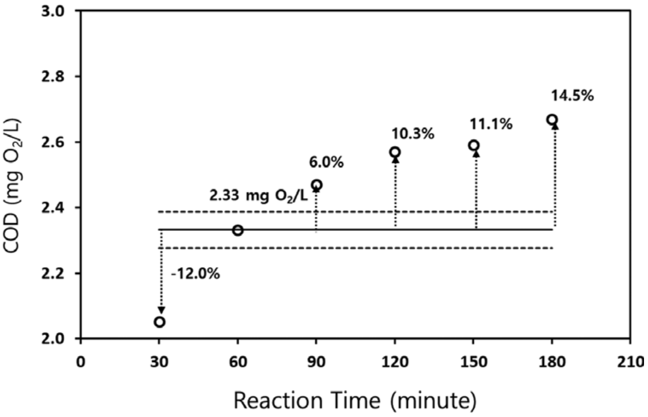

Fig. 3. Effect of reaction time on COD concentration. The solid line indicates the measured COD concentration using a 60-min reaction time (2.33 mg O_2/L). Two broken lines below and above the solid line are the standard deviation from the reaction conditions (± 0.057 mg O_2/L)

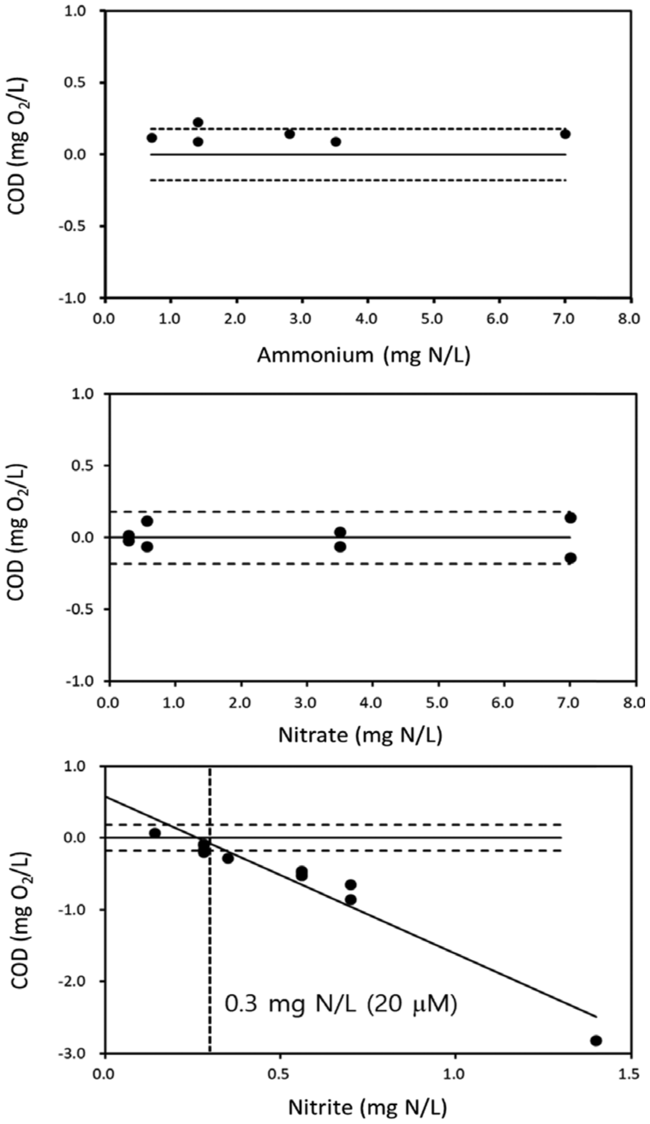

Fig. 4. Effect of a nitrogen compound on the measurement of COD concentration using the alkaline potassium permanganate method. The solid line indicates a blank COD concentration and the two broken lines indicate the detection limit of the KIOST modified method. The vertical broken line in the third panel indicates 0.3 mg N-NO_2/L in the sample

Effects of nitrogen compounds (nitrite, nitrate, and ammonia) in the sample

In APHA (2017), ammonia does not influence COD measurements of wastewater in the absence of significant free chloride ions. Nitrite exerts a COD of 1.1 mg O_2/mg NO_2. Because nitrite concentrations in water rarely exceed 1 or 2 mg nitrite, the interference is considered insignificant and is usually ignored. We investigated the influence of ammonia, nitrate, and nitrite on the measurement of COD by adding ammonia (up to 7.0 mg NH_4-N), nitrate (up to 7.0 mg NO_3-N), and nitrite (up to 1.4 mg NO_2-N) into DIW and artificial seawater. This study showed that the addition of ammonium using the alkaline potassium permanganate method resulted in a slight increase in COD concentration (0.14 ± 0.05 mg O_2/L), which was within the range of detection (Fig. 4). Similar to ammonium, the addition of nitrate showed that the mean COD concentration of blank samples was about 0.14 mg O_2/L, which was maintained within the detection limit of the KIOST modified MOF 2013-203 method (Fig. 4). The addition of nitrite showed no apparent difference from the addition of nitrate when added nitrite concentration was less than 0.3 mg N/L (or 20 μM), but a rapid decrease in COD concentration was observed when the nitrite concentration was > 0.3 mg N/L (or 20 μM). It was expected that COD would increase due to the oxidation of nitrite to nitrate by the oxidant ($KMnO_4$), but the COD decrease suggests the generation of oxygen during the digestion reaction. There was no proper explanation for the COD decrease in the presence of a high nitrite concentration in the sample. As such, COD data measured by the alkaline potassium permanganate method when the nitrite concentration is > 20 μM should be interpreted with caution.

Uncertainty related to reagent changes

The precision and accuracy of long-term COD measurements are closely related to the reagents used in the measurement. During continuous measurements, it is inevitable that the reagents ($KMnO_4$, $Na_2S_2O_3$, and starch solutions) will change for consecutive measurements, which may influence the precision and accuracy of COD measurements. We also estimated the uncertainty related to reagent changes by measuring the COD concentration of the same batch sample with newly prepared reagents and old reagents at the same time. On the basis of a matched-pair *t*-test, no apparent difference was caused by the change of reagents at the 95% confidence level (Table 3). The standard uncertainty caused by the change of reagents was calculated to be $0.20 / \sqrt{13} = 0.055$ mg O_2/L. Among the reagents used in the COD measurement, the starch solution does not participate in the reaction, unlike $KMnO_4$ or $Na_2S_2O_3$, and is simply used as the indicator for endpoint detection. But we experienced large variations in COD measurements when we used more than a week-old starch solution. As such, the starch solution may play a large role in the uncertainty of COD measurements.

Table 3. Comparison of COD concentration (mg O_2/L) from the different reagent set used for the measurement of various samples. Old reagents mean leftover reagents during the previous COD measurement and new reagents were newly prepared for consecutive COD measurements

Experiments	Samples	Old reagents	New reagents	Difference
1	1	2.33	2.26	0.07
	2	3.52	3.41	0.11
	3	3.56	3.22	0.35
2	1	2.33	2.46	-0.13
	2	2.25	2.35	-0.10
	3	2.40	2.50	-0.10
3	1	2.39	2.46	-0.07
	2	2.52	2.58	-0.06
4	1	2.30	2.35	-0.05
	2	2.43	2.41	0.02
5	1	2.22	2.41	-0.19
	2	3.57	3.06	0.51
	3	3.30	3.26	0.04
Mean ± s.d.				0.03 ± 0.20

Uncertainty related to the accuracy and precision of $Na_2S_2O_3$

As shown in equation (1), the concentration and volume of $Na_2S_2O_3$ is an important source of uncertainty in the calculation of COD concentration. The uncertainty related to the preparation of $Na_2S_2O_3$ is dependent on the accuracy of KIO_3 preparation and the endpoint determination of standardization. In the previous section, uncertainty related to the volume of $Na_2S_2O_3$ for the determination of COD was included in the uncertainty related to the reaction conditions. The uncertainty related to the estimation of an accurate $Na_2S_2O_3$ concentration may be included in the uncertainty related to the change of reagents. Thus, in this study, there was no separate estimation of uncertainty related to $Na_2S_2O_3$.

Expanded uncertainty and detection limit for COD determination in a seawater sample using the KIOST modified MOF 2013-203 method

The combined uncertainty related to COD determination using the KIOST modified method could be estimated by the combination of the uncertainty related to the reaction condition and the change of reagent as $\sqrt{0.0163^2 + 0.055^2}$ = 0.057 mg O_2/L. The COD detection limit using the KIOST modified MOF 2013-203 method was estimated from the standard deviation of the 10 repeated blank measurements at a 95% confidence level and was 0.057 × 3.14 = 0.18 mg O_2/L.

Consistency in COD measurements in seawater using the KIOST modified MOF 2013-203 method

To evaluate the consistency of COD measurements in seawater using the KIOST modified MOF 2013-203 method, we conducted COD measurements of sterilized seawater samples for 4–12 months. The long-term monitoring of three batch samples with different COD concentration levels (3.29, 3.15, and 2.42 mg O_2/L) showed a standard uncertainty of 0.20, 0.18, and 0.18 mg O_2/L, respectively (Table 4). Usually, the standard deviation is proportional to the concentration of the measuring parameter, and the standard deviations were similar with a mean value of 0.19 mg O_2/L, which was slightly higher than the expanded uncertainty of 0.11 mg O_2/L at a 95% confidence level ($k = 2$). The homogeneity and long-term stability of samples may be additional sources of uncertainty in addition to the expanded uncertainty. However, the detection limit mentioned earlier was 0.18 mg O_2/L. Thus, the variability observed in the COD concentrations of seawater samples

Table 4. Evaluation of long-term consistency using the KIOST modified MOF 2013-230 COD method with three seawater samples

Sample batches	Analysis periods	Mean (mg O_2/L)	Standard deviation	C.V (%)
A	2016.7.15~2017. 5.26	3.29	0.20	5.9
B	2016.7.22~2017. 7.20	3.15	0.18	5.9
C	2017.4.25~2017. 9.7	2.42	0.18	7.5

was mostly maintained within the detection limit of COD measurement with our current laboratory conditions and personal experience.

4. Conclusion

This study showed that there was no apparent difference in the modification of reaction vessels from the 250-mL round bottom flask with a graham condenser used in the standard procedure for COD measurements in MOF 2013-230 to a 100-mL beaker (no spout) with a watch glass for air condensation in the KIOST modified MOF 2013-203 method. In fact, this modification may enhance the efficiency of COD measurements by allowing a large number of samples (up to ~50 samples) to be analyzed at one time with the same reaction conditions. We estimated individual uncertainty related to sample volume transfer, reaction conditions, endpoint detection, reagent volume transfer, total amount of oxidant in the sample, expanded uncertainty, and detection limits. We also recommended estimating personal uncertainty related to the handling of the volume transfer and to make corrections for the estimated uncertainty for each person.

This study showed that the total amount of $KMnO_4$ solution needed for the reaction may change the efficiency of the reaction. Thus, we do not recommend changing the concentration and volume of the $KMnO_4$ solution from 0.025 to 0.01 N $Na_2S_2O_3$ to reduce uncertainty related to the titration. To reduce the uncertainty related to 0.025 N $Na_2S_2O_3$ during titration, we recommended improving the resolution of the instrument used and to enhance personal detection of the endpoint, which can be achieved by immersing the titration tip into the sample and the use of an anti-diffusion tip. Once these conditions have been established, it is very important to maintain the constant condition of a 1% starch solution. It is highly recommended that reference material is analyzed to ensure measurement comparability and to monitor the accuracy and precision of the measurement, but unfortunately, there is no commercially available COD reference material at this time. Alternatively, the control chart of blank measurements may provide very useful information for laboratory consistency of COD measurements such as a precise COD measurement within the laboratory when COD reference material is not available (Fig. 5).

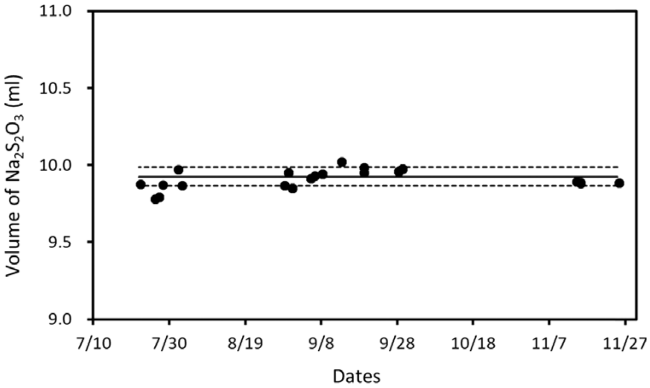

Fig. 5. Control charts of the 0.025 N $Na_2S_2O_3$ volume used in the blank titration during experimental periods (9.92 ± 0.052 mL). The solid line indicates the mean volume of 0.025 N $Na_2S_2O_3$, and two broken lines are the standard deviation

COD is a measure of organic pollutants in aqueous systems and provides more comprehensive information on organic pollutants than BOD and DOC. Thus, COD is widely used to monitor the organic contaminant levels in wastewater. It is a key parameter for TPLM regulations in highly developed coastal regions of Korea. The target water quality goals for Masan Bay, Suyoung Bay, and Shiwha Lake have been based on COD concentrations, which are < 2.5, 1.35, and 3.3 mg O_2/L, respectively. The expanded calculated uncertainty was much lower than the expected target measurement of heterogeneous samples for targeted COD concentrations in Masan Bay (0.75 mg O_2/L), Suyoung Bay (0.41 mg O_2/L), and Shiwha Lake (0.99 mg O_2/L) based on the Nordtest Report TR 537 using a parametric value (PV) and the relative deviation of 10% PV. The detection limit and expanded uncertainty (95% confidence level, $k = 2$) of the KIOST modified MOF 2013-230 method were 0.18 and 0.11 mg O_2/L, respectively. The expanded uncertainty from this study is slightly lower than that of Zhang and Guo (2007), who reported 0.2 mg O_2/L in the range of 0.0–4.0 mg O_2/L in a seawater sample. Therefore, use of the KIOST modified 2013-203 method may provide appropriate confidence in COD data for environmental management plans.

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