A study of students’ understanding of chemical oxide demand measurements at Teikyo University of Science:
A case study using Sumida River water

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Abstract
Representative Chemical Oxide Demand (abbreviated: COD) values of Sumida River's water and its variation factors of student's experiment of junior high and high school science teacher candidate course students (30 students) of the Department of School Education, Teikyo University of Science, were discussed in this article. First, effective method of measurement and calculated results were shown and then contributing factor of error was considered from student's reports and questionnaire results. Student's experimental results showed significant difference by tidal movement. As explanation of the relationship between chemical experiment and natural phenomenon would stimulate student's interests of science, student's surrounding living environment might be used for effective science education material for students. Each student group's COD measurement results showed significant error span. For getting better results, it would be necessary to accurate operation, such as solution adjustment and titration procedures. Though questionnaire results showed almost positive opinion, easier understandable textbook and appropriate explanation through experimental class would be necessary to give useful knowledge about chemistry to students.

Keywords: COD; student experiment; chemical education; Sumida River

I. Introduction

Science education dealing with our surrounding environment is useful not only to better understand each field of science but also for the multidisciplinary understanding of all fields of science and environmental issue[1-5]. In particular, the use of rivers for education is effective not only for better understanding of the connections between human life and natural resources but also for disaster education regarding river floods that threaten our lives[6,7]. Selecting and elaborating educational items from rivers would thus be applicable to education from elementary school to university[8].

The chemical oxide demand (COD) of river water, an indicator of contamination of artificial organic matter, is a useful value for understanding environmental pollution. An understanding of COD measuring and calculating processes is useful for understanding the accuracy and error ranges of reported data when determining the level of pollution and evaluating reported data.

In this study, representative methods of measuring and calculating COD using water from nearby Sumida River are shown as a case study of chemical experiments in junior high and high school science courses for teacher candidate students of the Department of School Education, Teikyo University of Science. Effective ways of measuring and calculating data and contributing factors of error were discussed based on students’ reports and questionnaire results, and the educational effects of using students’ surrounding living environment are discussed.

II. Definition and measurement methods of COD

1. What is COD?

COD is a chemical index of impurities in sea or river water by contaminating organic matter. COD is the oxygen milligram weight in one L of solution (mg/L), which is measured by a titration method using a strong oxidant, such as permanganic acid potassium salt ($KMnO_4$) or potassium bichromate ($K_2Cr_2O_7$), under strict chemical conditions. The environmental quality standard (lake) for conservation of life environment in basic law for environmental pollution control regulates the "type A" value, which can uses for water supply if less than 3mg oxygen per liter in solution (< 3mg/L). Other measured items, such as pH (6.5~8.5), suspended substance (SS<5mg/L), dissolved oxygen (DO>7.5mg/L), and coliform number (< 1000MPN/100ml) are regulated by the law.

2. COD measurement procedures for student experiments

COD measurement procedures for the students' chemical experiments are shown below[9]. These procedures were arranged for students to perform the handling more easily and to be more understandable.

Experiment 1: Concentration determination of potassium permanganate solution ($KMnO_4$ aq)

(a) Reagent adjustment 1: 2mmol/L $KMnO_4$ aq

The previously adjusted 10mmol/L $KMnO_4$ aq was diluted to one-fifth using a measuring cylinder and ion-exchanged water. Then, 250mL of the diluted solution was placed into a 300mL conical flask.

(b) Reagent adjustment 2: 5mmol/L $(COO)_2Na_2$ aq

Put the detailed measured 0.17g $(COO)_2Na_2$ into 250mL measuring flask, then add the ion exchanged water to the gauge line after the dissolved substance was completely dissolved.

(c) Concentration determination of $KMnO_4$ aq by $(COO)_2Na_2$ aq

After co-washing the burette with $KMnO_4$ aq and whole pipette by $(COO)_2Na_2$ aq three times, the $KMnO_4$ aq was placed into a burette, and the scale was recorded to the order of 0.01mL. Put the detailed measured 10mL $(COO)_2Na_2$ aq into a 200mL conical flask using a whole pipette. Put 40mL of ion-exchanged water and 5mL of sulfuric acid, which was pre-adjusted 3M, and warm the solution to 70~80°C. The endpoint of the redox reaction of the warmed $(COO)_2Na_2$ solution was measured three times using adjusted $KMnO_4$ aq. The range of titration error recommended to the students was within 0.1ml.

Experiment 2: Titration of sampled river water

(a) A 100mL measuring cylinder was co-washed with sampled water, which was filtrated by a 5A filter over three times. 100mL sampled water was placed into a 300mL conical flask.

(b) Put 10mL sulfuric acid, pre-adjusted at 3M and collected by graduated glass, into a 300mL conical flask, prepared at (a). Ten milliliters of $KMnO_4$ aq, which was pre-adjusted to 2mmol/L, into the conical flask using a burette as accurately as possible. The added volume should be noted as "v_1."

(c) Boiling stone was placed in a conical flask, heated moderately, and held for 5min after boiling. Quickly add 20mL sodium oxalate standard solution using a whole pipette.

(d) Confirm vanished red color with moderate shaking, quickly starting titration by 2mmol/L $KMnO_4$ aq. The added volume should be measured as correctly as possible, and the value of volume recorded as "v_2." This titration procedure has to be performed three times, and then the average value should be calculated.

(e) The blank test without sampled water was held under the same conditions as in Experiment 2.

COD was calculated with the below formula using the values of v_1 and v_2.

$$COD\ (O_2) = 80.0\times\{n_pC_p\times(v_1+v_2) - n_sC_s\times 20.00\}\ (mg/L)$$

n_p, n_s: number of reaction electrons $KMnO_4$ aq (n_p) and $(COO)_2Na_2$ (n_s)

C_p, C_s: number of molar concentrations of $KMnO_4$ aq (C_p) and $(COO)_2Na_2$ (C_s)

It's necessary to consider oxidation by nitrate, ferrous, chloride ions and Sulfide, when determine the current COD value as research.

III. Method

1. Outline of chemical experiment class of this study

The chemical experiment class is for junior students of the science course for junior high and high school in the Department of School Education, Teikyo University of Science. This chemical experiment lecture is a compulsory subject for students to obtain a teacher's license. By this point, students have been studying basic science lectures, such as physics, chemistry, biology, and geology, to obtain teachers'

Table 1 Main contents of students' experimental lecture in the Department of School Education, Teikyo University of Science

	Contents
No. 1	Orientation (schedule confirmation, division into small groups and attention for taking lecture)
No. 2	Assay of glass instrument for volume measure, such as measuring flask, whole pipette, cylinder, etc.
No. 3	Phase variation of CO_2 from solid, liquid, and gas phases
No. 4	pH titration by NaOH solution and sulfamic acid
No. 5	COD measurement in matter in our surrounding environment
No. 6	Thin-layer chromatography of amino acids and commercially available drug
No. 7	Absorption spectro-chemical analysis of copper ion
No. 8	Practical test

licenses in various prefectures for two and half years. Many students are taking advanced lectures.

The purpose of this lecture is to obtain basic skills and knowledge of chemical experiments, such as treating methods of glass instruments, solution preparation methods, and basic reaction procedures. In addition, how to avoid chemical hazard and treatment of waste materials and solutions are essential items for students to learn. Students are required to write bulletin reports for each experiment within two weeks.

The main contents of this experimental lecture are shown in Table 1.

2. Students

The number of students in the experimental class was 30, including 18 men and 12 women. These students were divided into two equal groups due to the constraints of facilities in the laboratory.

Each group was named A or B, which were divided into eight subgroups (1–8) composed of two students. While the A group students did experiments, the B group students had to prepare experimental notes, and vice versa for the B group student experiments.

3. Complete experimental procedure

a. Preparation of experimental note

Students were required to read and understand the textbook and make notes to prepare to perform the experiments smoothly. The note had to include the title, purpose, chemical basic principle, and procedure, and the professor checked it before beginning the experiment.

b. Experiment flow

b-1. Sampling of river water

Students went outside the building and did the following activities, sampling river water (1L), measuring the temperatures of both river water and air, checking flow direction and measuring its velocity, and observing the surface and surrounding environmental situation of the Sumida River.

b-2. Experimental procedures in laboratory

1) pH measurement and filtering using 5A filters were done to observe suspended substances after drying.
2) Preparation of $KMnO_4$ and $Na_2(COO)_2$ solutions and evaluation of $KMnO_4$ solution by $Na_2(COO)_2$ solution.
3) Oxidization of river water by $KMnO_4$ solution with 3M H_2SO_4 solution at the boiling condition for 5 minutes.
4) Titration of previously-treated river water by $KMnO_4$ solution.
5) Blank test by aforementioned same procedure without river water.

c. Summary and making a report

c-1. Confirmation of measured and calculated data in experimental note by professor.

c-2. Making reports in the fixed form by summarizing the experimental procedure, compiling data, and discussion.

4. Questionnaire for confirmation of students' understanding

Questionnaires to check the students' understanding level in both groups were conducted in the experimental class a week later. The brief content of the questions is as follows: (1) Level of COD understanding up to preparation of experiment note, (2) level of COD understanding after experiment, and (3) level of certainty (how many mistakes happened?) of experimental operations, (4) choice of difficult experimental specific procedures, (5) level of understanding of calculation procedure of COD, (6) educational influences by using students' surrounding living environment, and (7) impression of COD experiment. Detailed questions are shown in the Results section.

Table 2 Weather and river conditions, temperature, pH and SS of collected river water

Date	November 11th (neap)	November 16th (spring tide)
Weather	partly cloudy	cloudy
Temperature	18℃	22℃
River state	Dark green, turbid, suspended matter (small leaf and litter)	
Flow direction and speed (m/s)	Downstream, 0.35m/s*	Upstream, 0.26m/s*
River water temperature	19℃	20℃
pH	7.17*	7.29*
Suspended Substances	Mud and small organic matter	

* Average data measured by student groups

Table 3 COD calculation results of each student's group

November	9th		16th
Group No.	COD	Group No.	COD
A1	7.62	B1	5.41
A 2	6.56	B 2	4.99
A 3	7.32	B 3	unsubmitted*
A 4	7.90	B 4	unsubmitted*
A 5	8.51	B 5	4.89
A 6	7.26	B 6	6.05
A 7	7.32	B 7	5.81
A 8	unsubmitted*	B 8	4.79
average	7.50	average	5.34

* These groups could not get calculation results due to various problems.

IV. Results

1. Experiment condition

The experimental lectures were conducted on 9th and 16th in November, 2020. The weather and river conditions, temperature, pH, and SS of collected river water are shown in Table 2. The Sumida River showed moderate flow with dark green surface color on both days. The second day (16th) was a little windy. The characteristic difference of the river was that the flow direction was opposite on both days. It seems that the tidal movement of Tokyo Bay was the main reason for this.

2. COD calculation results of each group

The COD values calculated based on the data measured in the experiment, are shown in Table 3. Students performed experimental procedures diligently in cooperation with their partners. There was a significant difference in COD (2.16 on average) between the data for the 9th and 16th, mainly because of the difference in the flow direction of the Sumida River.

3. Student questionnaire results

Questionnaire items, alternatives, and the number of respondents (in parentheses) are shown below. To clarify students' opinions, a four-alternative questionnaire was used.

Question1: Did you understand the chemical meaning of COD at the step of preparation of experiment note?

1: completely understood (2), 2: partly understood (14), 3: understood little (13), 4: understood nothing (1)

Question2: Did you understand the chemical meaning of COD after taking part in the chemical experiment class?

1: completely understood (3), 2: partly understood (14), 3: understood little (11), 4: understood nothing (2)

Question3: Did you perform experimental work without a mistake? Without a mistake, you can score 100%.

1: completely (> 90%) well done (8), 2: occasional (50–90% well done) mistakes (18), 3: some (30~50%) mistakes (3), 4: frequent (< 30%) mistakes (1)

Question4: What kind of procedures did you find difficult in the experimental work?

1: sampling river water (3), 2: measuring temperature and pH (4), 3: solution adjustment (13), 4: titration operation (12), 5: treatment and operation of glass equipment (2), 6: cleanup (2)

Question5: Did you understand how to calculate the COD value?

1: completely understood (3), 2: partly understood (14), 3: understood little (13), 4: understood nothing (0)

Question6: Did you benefit from measuring your near environmental materials?

1: I benefited greatly (5), 2: I benefited somewhat (22), 3: I did not really benefit (3), 4: I did not benefit at all (0).

Question7: Please write your impressions of the experiment.

Students wrote both positive and negative opinions on their answer sheets. Representative positive opinions were that students could gain a deep understanding of COD through the experimental class, and that it increased their awareness of immediate chemical phenomena by using environmental materials familiar to the students, such as the Sumida River. Examples of negative opinions were complaints about excessive time versus a normal experimental lecture, and difficulty understanding the true meaning of COD through chemical experimental operations.

V. Discussion

1. The relationship between experimental procedures and causes of COD calculation errors

There was a significant difference in COD values (2.16 on average) between the data from November 9th and 16th, the major reason for this difference being that the flow direction of the Sumida River differed due to tidal movement. Sumida River's flow direction on November 9th was fair-current; on the other hand, on the 16th the flow direction was reversed. According to the tidal calendar, November 9th was neap tide and the 16th was spring tide. For confirmation of this, data on saline concentration and dissolved oxygen (abbreviated: DO), etc., should be measured, and it would be necessary to collect river water at some points in the downstream direction.

The main causes of error appearing from observing the students' experimental operations are as follows.

a. Operation accuracy of solution adjustment

Students had to measure the exact weight of sodium oxalate agent when they adjusted the standard reductant solution, and had to dilute the prepared permanganic acid potassium salt solution as an oxidant solution. Two steps of heating operations for completely oxidizing solutions, such as 80°C hot water bath treatment and 5min boiling operation with 3M sulfuric acid solution, would not have operated appropriately because of the students' lack of experience of chemical operation and poor experimental equipment, such as water bath, heater, tongs for heated beaker, etc. Experimental fractional errors would be accumulated from these operations requiring accuracy.

b. Titration accuracy

The dark-red permanganic acid potassium salt solution made it difficult for students to read the burette scale. Two steps with changing colors in titrated solutions caused students confusion in recognizing the end-point. On the other hand, after understanding the mechanisms of the chemical reaction, students' experimental accuracy was improved and scientific interest was stimulated.

c. To reduce errors

It was necessary to provide a detailed explanation of the accurate method of measuring the weight of agents, heating operations, and treatment of glass equipment before the students' operations. It was a good way for students to perform COD measurement experiments after the pH measurement experiment (Table 1, No. 4), which dealt with the same kind of experimental operations.

2. Questionnaire results

The average data of each question show below. These data were obtained by the calculation of students' average scores on their questionnaire answer sheets. For example, when five students chose alternative 1, which means the most positive opinion, and five chose alternative 2, the second most positive opinion, the average score can be calculated as $(1\times5+2\times5)/10 = 1.5$. Since this study adopted a four-alternative questionnaire, students were identified as having had a positive opinion about the question under the average score of 2.5, and a higher value identified as students had a negative opinion.

a. The average value of Question 1 for COD understanding up to the preparation of the experiment note was 2.43. This value indicates an intermediate understanding of COD experiments at the preparation stage. More easily understandable textbooks might be necessary to increase the understanding of students.

b. The average value of Question 2 for COD understanding after the experimental lecture was 2.40. Compared with Question 1, the slightly improved values mean that students' understanding levels remained intermediate even after the experimental lecture. It might be necessary to provide an easier and more understandable explanation before and during experimental operation.

c. The average value of Question 3 for experimental certainty regarding the experimental operations was 1.90. This value means that many students could operate experimental procedures without problems. Thus, this COD experiment seemed to be better suited for the students.
d. Major results of Question 4 about the difficulty of specific experimental procedures show that the rate of students selecting solution adjustment was 43%. As this was reported to be a difficulty in the COD experiment, it might be necessary to explain these operations in detail.
e. The average value for Question 5 on the level of understanding of the calculation procedure of COD was 2.33. This result shows a mismatch between the experimental operation and calculation procedures of COD. It might be necessary to provide a more detailed explanation to students to help them match the chemical operations and theory at the summarizing stage.
f. The average value for Question 6 for educational benefits of using the student's surrounding living environment was 1.93. This result showed that there were many benefits in stimulating students' scientific interests through using their surrounding living environment. The development of teaching materials that use students' surrounding living environments might provide a good opportunity to meet students' future needs after becoming teachers.
g. Question 7 concerned students' impressions of the chemical experiment, such as shorter hours of the experimental period and understandable explanations of the chemical theory and operations. Preparation of some solutions and equipment by assistants might be necessary to avoid excessive lecture times. As there were positive comments regarding the use of students' surrounding living environment, this kind of lecture might be useful for students who are teacher candidates. A combination of chemical experiments and the study of students' surrounding living environment might be effective not only for teacher candidate students but also for children who will be taught by them in near future.

3. Remediation points

Chemical experiments of COD measurements were performed over a long period at Teikyo University of Science. Questionnaire results showed that this subject, containing preparation, operation, and compiling results, was suitable for teacher candidate students. To ensure a more useful and understandable lecture, remediation points regarding the experimental operation are shown below.

a. As it took more time than the regular experimental lecture period, advance preparations, such as solution adjustment and glass equipment arrangement, might be needed to ensure sufficient time for chemical operation.
b. It might be necessary to prepare enough equipment, such as water baths and heaters for boiling, to save time.
c. Detailed observations of the filtrated substances should be performed to determine the relationship between the natural environment, such as geological and weather conditions, and the quality of river water.
d. DO, saline concentration, and biological oxygen demand (BOD) should be measured to better understand the influence of seawater on river water and its application in human usage.
e. Students should learn about pollution sources and methods for the purification of river water to improve its quality.

VI. Conclusion

The Sumida River COD measurement results for two experimental classes at a week interval showed significant differences due to tidal movement. Explanation of the relationship between chemical experiment's results and natural phenomena could stimulate students' interests in science. So, students' surrounding living environments could be used as effective science education materials for students.

Each student group's COD measurement results showed the maximum error span ranging from 1.26 to 1.96. To obtain better results, it would be necessary to perform accurate operations, such as solution adjustment and titration procedures. It is also necessary to prepare sufficient equipment and effective explanations through the experimental lecture.

The questionnaire results indicate an almost positive opinion that a more easily understandable textbook and appropriate explanation through experimental lectures would be necessary to obtain higher evaluations from students. Although most experimental operations could be performed appropriately, students felt solution adjustment and titration operations to be difficult. COD calculation procedures were thought to be difficult for many students. More detailed support for students when writing reports is required. Since students wrote positive opinions about the use of the surrounding living environments, the combination of indoor lectures and outdoor activities for learning science might be effective not only for students but also for the children whom they will teach in the near future.

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