Songklanakarin J. Sci. Technol.
47 (1), 1–7, Jan. – Feb. 2025

http://www.sjst.psu.ac.th

Original Article

The chloride mask in chemical oxygen demand determination of seawater and its validation

Meyliana Wulandari[1, 2*], Ashlasa Zata Zharfa[3], Denar Zuliandanu[4], Ahmad Syukri[4],
Nofrizal Nofrizal[5], and Pandian Bothi Raja[6]

[1] *Department of Chemistry, Faculty of Educational Science,*
State Islamic University (UIN) Syarif Hidayatullah, Jakarta, 15412 Indonesia

[2] *Department of Chemistry, Faculty of Mathematics and Natural Science,*
Universitas Negeri Jakarta, 13220 Indonesia

[3] *Department of Chemistry, Faculty of Science and Technology,*
State Islamic University (UIN) Syarif Hidayatullah, Jakarta, 15412 Indonesia

[4] *PT ITEC Solution, Bogor, West Java, 16135 Indonesia*

[5] *Department of Research and Development Centre, Lemigas, Jakarta, 12230 Indonesia*

[6] *School of Chemical Sciences, Universiti Sains Malaysia, Minden, Penang, 11800 Malaysia*

Received: 3 November 2023; Revised: 4 October 2024; Accepted: 1 November 2024

Abstract

Chemical Oxygen Demand (COD) is a water quality parameter that shows the amount of oxygen used to oxidize organic substances. Seawater high in chloride ions can have interference with direct COD measurements unless the chloride concentration is below 2,000 mg/L. In general, silver nitrate ($AgNO_3$) solution is used to mask the chloride interference in seawater. In this study, masking of chloride ions was carried out in seawater samples by using a 10.8% $AgNO_3$ concentration. The developed method was linear over the 0-50 ppm concentration range. The limits of detection (LOD) and quantification (LOQ) were found to be 0.944 mg/L and 0.962 mg/L, respectively. Meanwhile, the robustness was found to be 2.905 mg/L.

Keywords: chemical oxygen demand, chloride, seawater, validation of method

1. Introduction

Although often perceived as pretty ordinary, water is a most remarkable substance (Hermawan *et al.*, 2023). Life could not have evolved without water because for drinking, washing, and cooking we need water (Hasanah *et al.*, 2020). Oxygen demand is an important parameter indicating the concentration of organic contaminants because the degradation of organic compounds requires oxygen. Three parameters can be used for this purpose, namely the chemical oxygen demand (COD), biological oxygen demand (BOD), and total organic carbon (TOC). Among these, COD has advantages in speed and ease of determination (Carbajal-Palacios, Balderas-Hernández, Roa-Morales, & Ibanez, 2017). COD is the number of oxygen equivalents required to oxidize the organic components in a sample (Li, Luo, He, Xu, & Lyu, 2018; Yao, Wang, & Zhou, 2014).

---

*Corresponding author
Email address: meylianawulandari@uinjkt.ac.id

COD values are usually determined by oxidizing organic matter with potassium dichromate ($K_2Cr_2O_7$) as the source of oxygen, the oxidizing agent (Wang, Wang, & Dong, 2018). The oxygen consumed is equivalent to the dichromate required to oxidize the water sample. The dichromate ion in this reaction will be reduced to a chromate ion. The COD value is then determined by looking at the residual dichromate ion amount or the amount of chromate ions formed by completed reactions (Yang, Liu, & Yang, 2009). However, COD measurement can be perturbed by oxidized inorganic compounds, including ferrous, sulfide, manganese, nitrite, ammonia, and halogen ions. Such interference can result in negative errors. Usually, wastewater and seawater have high chloride concentrations (Kolb, Bahadir, & Teichgräber, 2017). This research aims to mask high Cl^- levels in seawater samples so that COD can be measured directly.

The principle of COD measurement is the oxidation of organic pollutants by dichromate. If there are Cl^- ions, oxidation is disrupted because dichromate prefers Cl^- over organic pollutants, so a masking agent is needed for Cl^- (Cardona, Park, & Lin, 2016; Geerdink, Sebastiaan van den Hurk, & Epema, 2017). Several studies were successful in preventing Cl^- interference: mercury sulfate ($HgSO_4$), as a masking agent for industrial wastewater, was added to pure samples at a ratio of 10:1 at 150-175 rpm, and centrifugation for 20 minutes effectively resulted in an estimated sample COD of 35,000 mg/L (Gnanavelu, Shanmuganathan, Deepesh, & Suresh, 2021). The main disadvantage of mercury sulfate is that it is very toxic, particularly when used in large quantities. Mercury salts in the waste solution are difficult to dispose of and will cause secondary environmental pollution.

An earlier study on silver sulfate (Ag_2SO_4) was able to achieve an efficiency of 94% and fulfilled the Hg-free test efficiency of 96%. This mercury-free COD test is feasible for water samples with a maximum chloride concentration of 500 mg/L. Meanwhile, the average seawater chloride content is 19,400 mg/L. Hence, this method is considered less accurate when measuring seawater samples (Kishimoto & Okumura, 2018). Based on previous research, $AgNO_3$ is able to precipitate Cl^- at more than one thousand ppm in the seawater matrix, which is a high Cl^- level (Pertiwi, Purwanti, & Widagdo, 2022).

COD measurement can be carried out using open or closed reflux. Open reflux is not chosen because it requires a longer time (Yadvika, Yadav, Sreekrishnan, Satya, & Kohli, 2006). The titrimetric method has been used with the help of microwave digestion, but the results are less accurate than those of spectrometry (Chen, Tzeng, Tien, & Wu, 2001). Therefore, in this research, $AgNO_3$ will be used with the closed reflux method and then measured with the spectrometric method (Santos *et al.*, 2022). The parameters studied include concentration and volume of Ag^+ and centrifugation time to reduce the Cl^- concentration in seawater samples. Then, it is necessary to validate the developed or modified procedure. Method validation has been carried out including determinations of linearity, precision, accuracy, LOD, LOQ, and robustness.

2. Materials and Methods

The apparatus used in this study includes glassware commonly used in chemistry laboratories and a centrifuge tube, water quality meter, COD reactor, digestion tube, cuvette, and UV-Vis Thermo-Scientific Genesys 20 Visible Spectrophotometer. The following chemical were purchased from Merck, Darmstadt, Germany: $AgNO_3$, K_2CrO_4, $K_2Cr_2O_7$, Ag_2SO_4, $HgSO_4$, H_2SO_4, and $HOOCC_6H_4COOK$ (potassium hydrogen phthalate/PHP). Sea water sampling was carried out in Muara Angke, Pluit, Penjaringan, and North Jakarta City, Indonesia.

2.1 Determination of the initial chloride concentration in seawater samples

The Cl^- ion determination was done after measuring seawater samples' initial pH, electrical conductivity, and salinity. Seawater was diluted 1000 fold. The sample was then put into a 250 mL Erlenmeyer flask, and 1 mL of K_2CrO_4 was added as an indicator. Determination of chloride concentration was done by argentometric titration with a standardized 0.0141 N $AgNO_3$ solution until a reddish-yellow colour was formed as the endpoint (Rahmawati & Tanjung, 2020). The following calculation gives the chloride concentration:

$$\text{Cl (mg/L)} = \frac{(A-B) \text{ x } N \text{ x } 35450}{V} \text{ x DF} \tag{1}$$

A = $AgNO_3$ volume used when titrating the sample
B = $AgNO_3$ volume used during blank titration
N = Normality of $AgNO_3$ solution
V = Sample volume
DF = Dilution factor

2.2 Digestion solution and potassium hydrogen phthalate (PHP) preparation

The digestion solution was prepared by adding 1.022 g of $K_2Cr_2O_7$, which had been dried at 150°C for 2 hours, into 500 mL of distilled water (Zupančič & Roš, 2012). Then, 167 mL of concentrated H_2SO_4 and 33.3 g of $HgSO_4$ were added to the solution. The solution was homogenized, cooled at room temperature, and then diluted to 1000 mL. PHP standard solution was prepared by grinding PHP and then drying it to a constant weight at 110°C. A 425 mg amount of PHP was dissolved in organic free water and measured in a 1000 mL volumetric flask (stored at 4±2 °C), and this can be used for up to 1 week if there is no microbial growth. PHP standard solutions were made with 0, 5, 20, 40, and 50 mg/L concentrations.

2.3 Un-spiked and spiked samples

The Cl^- ion concentration below 2,000 mg/L was pipetted for the un-spiked sample to get the supernatant. It was transferred into a 10 mL vial to precipitate the remaining solids without being filtered. The spiked sample was prepared by adding known analyte solutions. A 4 mL amount of 500 mg/L of PHP standard solution was pipetted into a 100 mL flask. The flask was then calibrated using seawater to prepare the sample using PHP with a COD equivalent of 20 mg/L. The Ag^+ was added to the solution and centrifuged at the optimum conditions. The centrifuged supernatant was pipetted and transferred to a vial without being filtered.

2.4 Digestion process

A 2.5 mL sample was pipetted into the digestion tube. Digestion and sulfuric acid solutions were added in amounts of 1.5 and 3.5 mL, respectively. The tube was closed, and the solution was homogenized before finally placing it in the COD reactor, which had been heated at 150°C for 2 hours.

2.5 Data analysis

After digestion process, samples were measured for absorbance using a UV-Vis spectrophotometer at a wavelength of 420 nm. The linearity of response was assessed from correlation of concentration (x-axis) and absorbance (y-axis). The slope (s), intercept (i), and correlation coefficient (r) were calculated. For measuring the precision, measurements were repeated seven times, and the analysis results assessed were the standard deviation and the relative standard deviation RSD (Equation 2). The results obtained were compared with Horwitz RSD as the standard.

$$\% \text{ RSD} = \frac{SD}{\bar{x}} \text{ x } 100\% < (0,67)^{21-0,\ 5\log C} \qquad (2)$$

Where

SD = standard deviation

$\bar{x}$ and C = mean

Accuracy is obtained by recovering the spiked sample concentration from the un-spiked sample (Equation 3).

$$\%R = \frac{\text{Concentration}_{\text{obtained}}}{\text{Concentration}_{\text{theory}}} \qquad (3)$$

Limit of Detection (LOD) and Limit of Quantification (LOQ) were determined from blank measurements (Armbruster & Pry, 2008). The LOD is the concentration of the blank average plus three times the standard deviation, while the LOQ is obtained from the average blank and ten times the standard deviation (Saadati *et al.*, 2013). LOD and LOQ are defined by Equations 4 and 5.

$$\text{LOD} = \bar{x} + 3\text{SD} \qquad (4)$$

$$\text{LOQ} = \bar{x} + 10\text{SD} \qquad (5)$$

3. Results and Discussion

3.1 The initial Cl^- concentration

$AgNO_3$ is used as a chloride masking agent in seawater samples. The initial seawater samples have a pH of 7.32 and an electrical conductivity of 36.8 mS/cm. The data shows that seawater samples meet the criteria for average seawater having a pH of 7 – 8.5, and electrical conductivity of saltwater in the range of 15 – 50 mS/cm (Assiry, Gaily, Alsamee, & Sarifudin, 2010).

The initial Cl^- concentration was determined by the Mohr method, with dilute K_2CrO_4 used as the indicator. Possible reactions that occur during the titration are as follows:

$$\text{NaCl (aq)} + \text{AgNO}_3\text{ (aq)} \rightarrow \text{AgCl (s)} + \text{NaNO}_3\text{ (aq)} \qquad (6)$$

$$2\ \text{AgNO}_3\text{ (aq)} + \text{K}_2\text{CrO}_4\text{ (aq)} \rightarrow \text{Ag}_2\text{CrO}_4\text{ (s)} + 2\ \text{KNO}_3\text{ (aq)} \qquad (7)$$

The analyte forms a white silver chloride precipitate based on the first reaction above. Then, the endpoint of the titration is reached when a red colour has formed. $AgNO_3$ as the titrant has gone through a standardization process. In this research, NaCl solution was used because it is a primary standard solution with high purity and stability and is not easily oxidized. The Cl^- concentration was 18,443.22 ppm or 1.8%.

3.2 Optimization of chloride masking

The three variables Ag^+ concentration (3.6%; 7.2% or 10.8%), the volume of Ag^+ 1.5 mL (orange bar) or 3.0 mL (blue bar), and centrifugation time (10, 15, or 25 minutes) were optimized. Figure 1A displays the decrease in Cl^- concentration by adding an Ag^+ masking solution with a concentration of 3.6%. Adding 1.5 mL of Ag^+ masking solution resulted in the weakest reduction in Cl^-. It can be seen that the Cl^- is still high at 13,800, 12,570, and 12,430 ppm in 3.6% Ag^+; at 11,350; 11,250, and 10,750 ppm in 7.2% Ag^+; and at 7,800; 7,500, 7,400 ppm in 10.8% Ag^+. Meanwhile, with 3 mL of Ag^+ the Cl concentration decreased. Using 3 mL of Ag^+ as a masking solution was the best choice.

Figure 1B shows the reduction of Cl^- in seawater using 7.2% of Ag^+. When the volume of Ag^+ used was increased from 1.5 mL (orange bar) to 3 mL (blue bar), there was an increase in the ability of Ag^+ to reduce Cl^-. An Ag^+ volume of 3 mL was better than 1.5 mL in reducing Cl^- levels. This shows that the effect of volume on the reaction rate in this study is more significant when compared to the effect of concentration. Reducing the Cl^- using 3 mL of Ag^+ at 7.2% is still better than 1.5 mL. This is possibly because more collisions between molecules occur with increased volume. However, the Cl^- was still above 2,000 mg/L. After adding 3 mL Ag^+ at 10.8%, the Cl^- concentration was reduced to below 2,000 mg/L. It can be seen in Figure 1C that under these conditions, with a centrifugation time of 10, 15, and 25 minutes, the Cl^- was 1,400, 800, and 390 mg/L. The longer centrifugation time significantly affected the decrease in Cl^-. Silver chloride (AgCl) was more completely separated from the supernatant as the centrifugation time was longer.

3.3 Validation of methods

A linearity determination was carried out to assess the relationship between analyte concentration and absorbance (Moosavi & Ghassabian, 2018). This linearity determination used 10-50 mg/L potassium hydrogen phthalate (PHP) concentrations as the COD standard solution. The standard PHP solution, when oxidized in the digestion process by dichromate, produces Cr^{3+}. The absorbance of a standard COD solution that is less than or equal to 90 mg/L is determined by the remaining Cr^{6+}.

Based on Figure 2, it can be seen that the higher the concentration of PHP, the lower the absorbance. The resulting curve is decreasing with R^2 of 0.9953. So, the higher the concentration of PHP, the less there are residual Cr^{6+} ions from potassium dichromate because they have been used in oxidation. This agrees with previous research (Cadena *et al.*,

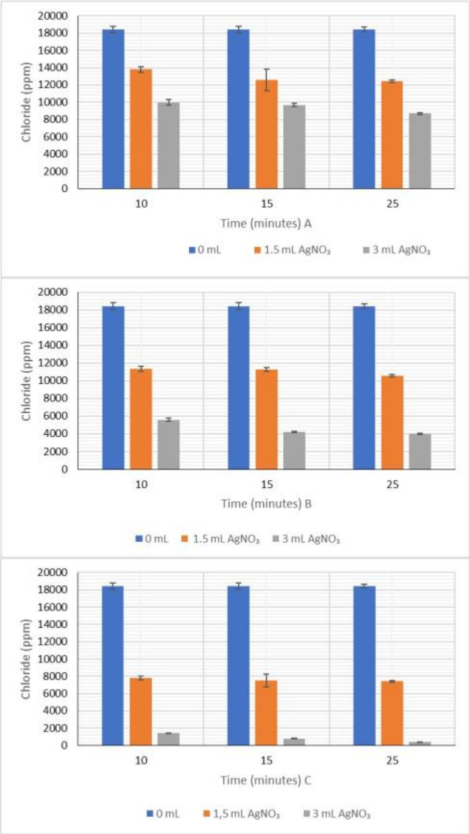

Figure 1. Optimization of Cl^- reduction with Ag^+ solutions at 3.6% (A), 7.2% (B), and 10.8% (C) with the volume of Ag^+ 0 (blue bar), 1.5 mL (orange bar) and 3 mL (grey bar)

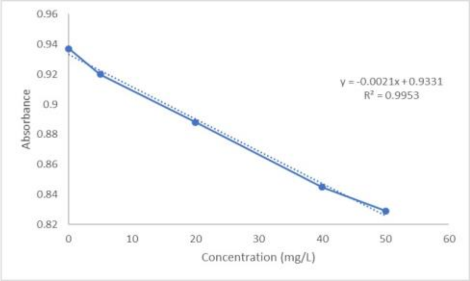

Figure 2. Potassium hydrogen phthalate (PHP) standard linear regression fit

2011).

Precision is divided into three aspects: intra-repeatability, internal, and external reproducibility. Repeatability measures the diversity of test results on the same samples, analysts, determination methods, materials, equipment, and laboratories in a short time. External reproducibility uses different laboratories and analysts, while internal reproducibility precision can be carried out by one analyst within the same laboratory. In this research, the precision focus chosen is intra-reproducibility. Determinations are done in the same laboratory and test samples but with different methods, chemicals, equipment, analysts, and time.

The precision related measurements were repeated seven times. Then, the calculation of the standard deviation (SD) and relative standard deviation (%RSD) across the samples was done (Figure 3 and Table 1). The requirement for precision acceptance is by a comparison between %RSD and 2/3 %CV Horwitz, where %RSD must be less than or equal to 2/3 %CV Horwitz (Juliasih, Hidayat, Pirdaus, & Rinawati, 2021).

The calculation the standard deviation follows applicable statistical theory, while the %RSD is obtained by dividing the standard deviation by the average value. The %RSD obtained from the test results is then evaluated to ensure it does not exceed the precision acceptance limit. The limits used in precision tests generally use the William Horwitz equation or %CV Horwitz namely %CV Horwitz = 2 (1-0.5 log C). Because the concentration is expressed in mg/L (ppm), it must be multiplied by 10^{-6} when entered into the Horwitz equation.

Accuracy is obtained by calculating the recovery %. It can be calculated by comparing the difference between the measured analyte and target concentrations. The measured concentration was obtained by measuring the spiked sample concentration (the sample with the addition of 20 ppm PHP). The results of the accuracy study can be seen in Figure 4. According to the concentration measurement results for each measured and target sample, the recovery found was 97.96% (Table 2). These results indicate that the test method used has high accuracy and is within the validation acceptance range (85-115%) (Gniazdowska, Goch, Giebułtowicz, & Rudzki, 2022).

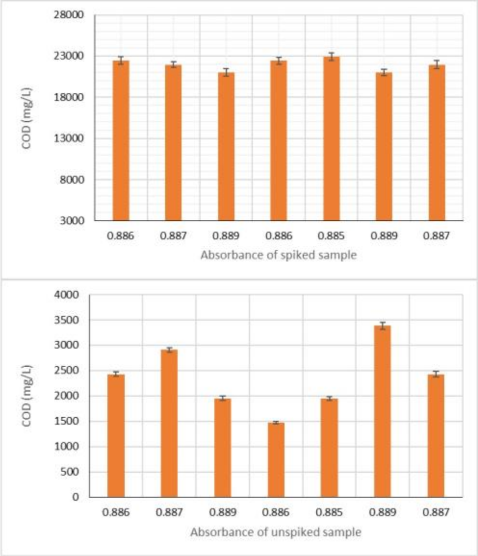

Figure 3. Spiked and un-spiked sample precision studies

Table 1. Precision study of spiked and un-spiked samples

	Spiked	Un-spiked
Average of absorbance	0.887	0.928
Average of concentration (mg/L)	21.952	2.361
Standard deviation (SD)	1.527×10^{-3}	1.345×10^{-3}
%RSD	1.722×10^{-1}	1.449×10^{-1}
%CV Horwitz	10.051	14.059
2/3 %CV Horwitz	6.7006	9.3731
Conclusion	acceptable	acceptable

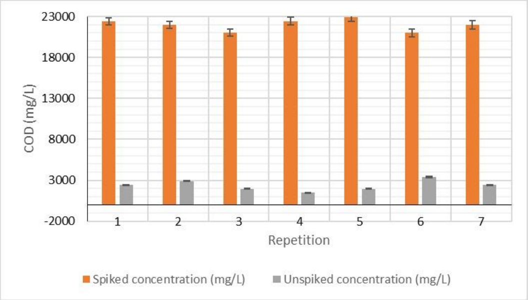

Figure 4. A comparison between spiked and un-spiked cases for accuration determination

Table 2. A comparison of spiked and un-spiked sample concentrations for accuration study

The average of spiked concentration (C_1)	21.952 mg/L
The average of unspiked concentration (C_2)	2.361 mg/L
C_1-C_2	19.592 mg/L
%Recovery	97.96%
The acceptance requirement	85-115%
Conclusion	Acceptable

The limit of detection (LOD) is the lowest detectable concentration of analyte. Meanwhile, the LOQ is the lowest concentration that can be measured quantitatively. The calculation (Table 3) shows that the limit of detection (LOD) is 0.944, which indicates that the UV-Vis spectrophotometer instrument can still read the smallest value of the analyte contained in the sample. The quantification limit (LOQ) is 0.962. It shows that the analyte can be quantified precisely and accurately if its level is above 0.962 mg/L.

Table 3. LOD and LOQ analyses

The average of blank concentration (mg/L)	0.937
Deviation standard	0.002573
LOD (mg/L)	0.944
LOQ (mg/L)	0.962

Robustness of a method relates to its capability to remain unaffected by small changes and variations of parameters and still perform well under normal conditions. The robustness test was carried out by varying changes in Ag^+ volume. It was done because Ag^+ volume contributed the most to chloride masking. Thus, the volume of Ag^+ used during optimization was initially 3 mL, reduced by 0.2 mL to 2.8 mL. Besides the volume of Ag^+, the Ag^+ concentration and centrifugation time were also varied. The concentration of Ag^+ used was 10% with a centrifugation time of 20 minutes. The absorbance of the robustness sample was measured using a UV-Vis spectrophotometer to determine the chloride concentration after being treated with the variations.

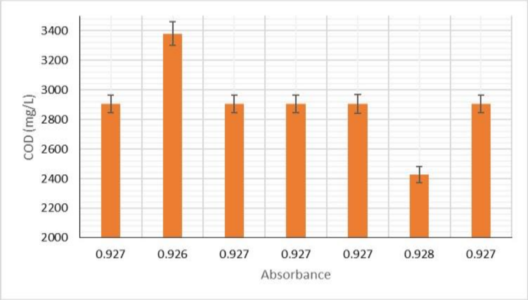

Figure 5. The robustness of sample concentration measurements

Table 4. F- and t-test analyses for robustness

	F-test	T-test
Variable total (k)	4	-
Repetitions (n)	7	7
The average of Cl^- un-spiked sample (X_1)	2.361 mg/L	2.361 mg/L
The average of Cl^- sample robustness (X_2)	2.905 mg/L	2.905 mg/L
The combination of standard deviation	-	0.49
Standard deviation of un-spiked sample (SD_1)	0.64	-
Standard deviation of robustness sample (SD_2)	0.27	-
$F_{calculated}$ (SD_1^2/SD_2^2)	5.43	
F_{table} ($F_{(0.05;3;3)}$)	9.27	
$T_{calculated}$	-	2.06
T_{table}	-	2.17
The conclusion of F dan T-test	$F_{calculated} \leq F_{table}$ Acceptable	$T_{calculated} < T_{table}$ Acceptable

The COD concentration of the robustness sample was measured on seven repetitions, as shown in Table 4 and Figure 5. The average measurement was 2.905 mg/L. This value has a difference of 0.544 mg/L with the un-spiked sample, which has an average COD measurement of 2.361 mg/L. After obtaining these results, an analytical assessment of the precision and accuracy should be conducted to evaluate methodological changes. The F-test is commonly used to determine the precision of two independent data sets.

Table 4 shows that the F-test for precision is carried out by comparing the results of the squares of the two standard deviations of the test repetition results, both the results from the un-spiked sample and the robustness sample. The two measured types of repetition results have a precision that is not significantly different if the value of F-calculated ≤ F-table at the commonly used confidence level of 95% (α = 0.05). Through these provisions, the value of robustness research was obtained from table F for (0.005;3;3), which was 9.28, while for F-count, the value was 5.44. The F-test results show that the two conditions' precision is accepted because F-count ≤ F-table.

The response effects on accuracy were also assessed to analyze the robustness test results (Table 4). Accuracy response can be studied by comparing the dataset of repeated test results through the t-test. So, the value for $t_{(0.05;12)}$ is 2.18, while the t-calculated obtained is 2.07. The t-test shows that the two conditions' accuracy is accepted because t-calculated ≤ t-table at a 95% confidence level (α=0.05). Robustness tests indicate that the test method is not affected by small changes and variations but continues to perform well. It is supported by the results of the F-test for precision and the t-test for robustness of sample accuracy.

4. Conclusions

Chloride in the seawater sample was successfully masked within the lower range from 18,443 mg/L to 390 mg/L. The optimum conditions for $AgNO_3$ masking were a concentration of 10.8% of the $AgNO_3$ solution, a volume of 3 mL, and a centrifugation time of 25 minutes. It has a Cl^- concentration below 2,000 mg/L. The linearity test gave a correlation coefficient of 0.9953; the precision parameters had yield %RSD of 0.17% for spiked samples and 0.14% for un-spiked samples; the accuracy showed that the spiked sample with a COD concentration of 21.95 mg/L and the un-spiked sample of 2.361 mg/L produced a recovery % of 97.96%; the limits of detection (LOD) and quantification (LOQ) obtained were 0.944 mg/L and 0.962 mg/L respectively; and the robustness resulted in a COD concentration of 2.905 mg/L with precision and accuracy responses not significantly different through the f-test and t-test. Each validation test gave values within acceptable limits.

Acknowledgements

The author thanks the PT. ITEC Solution for the support and facilities gained for this research.

References

Armbruster, D. A., & Pry, T. (2008). Limit of blank, limit of detection and limit of quantitation. *The Clinical Biochemist. Reviews, 29 Supplmental 1*(August), S49-52. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/18852857%0Ahttp://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=PMC2556583

Assiry, A. M., Gaily, M. H., Alsamee, M., & Sarifudin, A. (2010). Electrical conductivity of seawater during ohmic heating. *Desalination*, *260*(1–3), 9–17. doi:10.1016/j.desal.2010.05.015

Cadena, P. G., Araújo, A. N., Montenegro, M. C. B. S. M., Pimentel, M. C. B., Filho, J. L. L., & Silva, V. L. (2011). Physical-chemical parameters and validation of a colorimetric method for deoxycholic and ursodeoxycholic acids: Kit reagent and optical sensor. *Chemistry and Physics of Lipids*, *164*(2), 99–105. doi:10.1016/j.chemphyslip.2010.11.004

Carbajal-Palacios, P., Balderas-Hernández, P., Roa-Morales, G., & Ibanez, J. G. (2017). A greener UV and peroxide-based chemical oxygen demand test. *Water, Air, and Soil Pollution*, *228*(8). doi:10.1007/s11270-017-3470-x

Cardona, I., Park, H. Il, & Lin, L.-S. (2016). Improved COD measurements for organic content in flowback water with high chloride concentrations. *Water Environment Research*, *88*(3), 210–216. doi:10.2175/106143016x14504669767571

Chen, S. C., Tzeng, J. H., Tien, Y., & Wu, L. F. (2001). Rapid determination of Chemical Oxygen Demand (COD) using focused microwave digestion followed by a titrimetric method. *Analytical Sciences*, *17*(4), 551–553. doi:10.2116/analsci.17.551

Geerdink, R. B., Sebastiaan van den Hurk, R., & Epema, O. J. (2017). Chemical oxygen demand: Historical perspectives and future challenges. *Analytica Chimica Acta*, *961*, 1–11. doi:10.1016/j.aca.2017.01.009

Gnanavelu, A., Shanmuganathan, T. S., Deepesh, V., & Suresh, S. (2021). Validation of a modified procedure for the determination of chemical oxygen demand using standard dichromate method in industrial wastewater samples with high calcium chloride content. *Indian Journal of Science and Technology*, *14*(29), 2391–2399. doi:10.17485/ijst/v14i29.1412

Gniazdowska, E., Goch, W., Giebułtowicz, J., & Rudzki, P. J. (2022). Replicates number for drug stability testing during bioanalytical method validation—An experimental and retrospective approach. *Molecules*, *27*(2). doi:10.3390/molecules27020457

Hasanah, U., Mulyati, A. H., . S., Widiastuti, D., Warnasih, S., Syahputri, Y., & Panji, T. (2020). Development of COD (Chemical Oxygen Demand) analysis method in waste water using uv-vis spectrophotometer. *Journal of Science Innovare*, *3*(2), 35–38. doi:10.33751/jsi.v3i2.3007

Hermawan, S., Tjahyana, A. J. T., Utomo, K. P., Wahyuni, N., Tiewanto, P., Limantara, I. R., & Huidiyanto, D. (2023). Brackish water treatment in Sidoarjo area (East Java Indonesia) using Reverse Osmosis (RO). *AIP Conference Proceedings*, *2691*. doi:10.1063/5.0118443

Juliasih, N. L. G. R., Hidayat, D., Pirdaus, P., & Rinawati, R. (2021). Verification of the determination method of dissolved metal content using ICP-OES and its application for river water in Bandar Lampung City. *Jurnal Kimia Sains Dan Aplikasi*, *24*(1), 29–36. doi:10.14710/jksa.24.1.29-36

Kishimoto, N., & Okumura, M. (2018). Feasibility of mercury-free Chemical Oxygen Demand (COD) test with excessive addition of silver sulfate. *Journal of Water and Environment Technology*, *16*(6), 221–232. doi:10.2965/jwet.18-016

Kolb, M., Bahadir, M., & Teichgräber, B. (2017). Determination of Chemical Oxygen Demand (COD) using an alternative wet chemical method free of mercury and dichromate. *Water Research*, *122*, 645–654. doi:10.1016/j.watres.2017.06.034

Li, J., Luo, G., He, L. J., Xu, J., & Lyu, J. (2018). Analytical approaches for determining chemical oxygen demand in water bodies: A Review. *Critical Reviews in Analytical Chemistry*, *48*(1), 47–65. doi:10.1080/10408347.2017.1370670

Moosavi, S. M., & Ghassabian, S. (2018). Linearity of calibration curves for analytical methods: A review of criteria for assessment of method reliability. *Calibration and Validation of Analytical Methods - A Sampling of Current Approaches*. doi:10.5772/intechopen.72932

Pertiwi, T. S., Purwanti, T., & Widagdo, N. (2022). Improving quality of COD analysis using $AgNO_3$ for wastewater samples with high chloride content. *IOP Conference Series: Earth and Environmental Science*, *1098*(1). doi:10.1088/1755-1315/1098/1/012038

Rahmawati, I., & Tanjung, Y. P. (2020). Determination of chlorine on brewed robusta coffee (Coffea canephora var. Robusta) with V60 method. *JKPK (Jurnal Kimia Dan Pendidikan Kimia), 5*(3), 318. d doi:10.20961/jkpk.v5i3.46746

Saadati, N., Abdullah, M. P., Zakaria, Z., Sany, S. B. T., Rezayi, M., & Hassonizadeh, H. (2013). Limit of detection and limit of quantification development procedures for organochlorine pesticides analysis in water and sediment matrices. *Chemistry Central Journal*, *7*(1), 1–10. doi:10.1186/1752-153X-7-63

Santos, L. S. R. dos, Tamashiro, J. R., Zanelotti, D. S., Silva, L. H. P., Paiva, F. F. G. de, Oliveira, D. V. M. de, & Kinoshita, A. (2022). Treatment of agro-industrial effluents with silver nanoparticles to reduce chemical oxygen demand and microorganisms. *Cleaner Waste Systems*, *3*(September), 100058. doi:10.1016/j.clwas.2022.100058

Vahidipour, M., Raeisi, E., & van der Zee, S. E. A. T. M. (2021). Active saltwater intrusion of shrinking Bakhtegan-Thask Lakes in South Iran threatens the freshwater resources of coastal aquifers. *Journal of Hydrology: Regional Studies*, *34*(September 2020), 100790. doi:10.1016/j.ejrh.2021.100790

Wang, J. P., Wang, X. H., & Dong, Q.-H. (2018). Analysis and discussion on the formula of classical monitoring method for Chemical Oxygen Demand (CODcr). *Journal of Education and Practice*, *9*(23), 93–97. Retrieved from www.iiste.org

Yadvika, Yadav, A. K., Sreekrishnan, T. R., Satya, S., & Kohli, S. (2006). A modified method for estimation of chemical oxygen demand for samples having high suspended solids. *Bioresource Technology*, *97*(5), 721–726. doi:10.1016/j.biortech.2005.04.013

Yang, Q., Liu, Z., & Yang, J. (2009). Simultaneous determination of Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD5) in wastewater by near-infrared spectrometry. *Journal of Water Resource and Protection*, *01*(04), 286–289. doi:10.4236/jwarp.2009.14035

Yao, N., Wang, J., & Zhou, Y. (2014). Rapid determination of the chemical oxygen demand of water using a thermal biosensor. *Sensors (Switzerland)*, *14*(6), 9949–9960. doi:10.3390/s140609949

Zupančič, G. D., & Roš, M. (2012). Determination of chemical oxygen demand in substrates from anaerobic treatment of solid organic waste. *Waste and Biomass Valorization*, *3*(1), 89–98. doi:10. 1007/s12649-011-9087-1