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EFFECTS OF COOLING TIME AND MERCURY CONCENTRATION ON CHEMICAL OXYGEN DEMAND (COD) ANALYSIS IN DOMESTIC WASTEWATER SAMPLES

Romsan Madmanang[a], Thaniya Wangprasert[b], Suparat Eiamtako[b], Tongchai Sriwiriyarat[b*]

[a]Faculty of Science Technology and Agriculture, Yala Rajabhat University, Yala, 95000, Thailand
[b]Department of Chemical Engineering, Faculty of Engineering, Burapha University, Chonburi, 20131, Thailand

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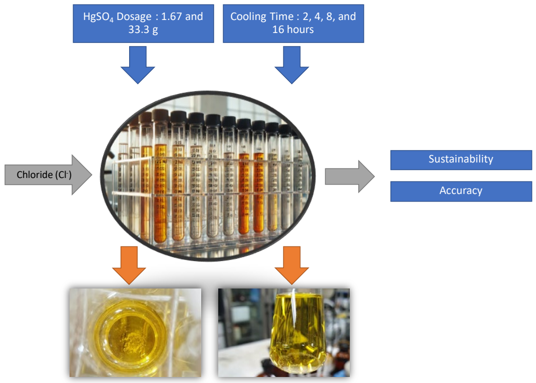
*Corresponding author
sriwiri@buu.ac.th

Graphical abstract



Abstract

Chloride (Cl^-) interferes with Chemical Oxygen Demand (COD) measurement, necessitating the use of mercury sulfate ($HgSO_4$) to eliminate chloride. Typically, 33.3 g of $HgSO_4$ is required. Excess $HgSO_4$ introduces hazardous waste, and the effect of cooling time on COD accuracy is unexplored. This study examines the effects of cooling time and $HgSO_4$ dosage on the accuracy of COD analysis. Water samples with a constant COD concentration were analyzed using the closed reflux method under varying chloride concentrations, cooling times, and $HgSO_4$ dosages. The findings reveal that a reduced $HgSO_4$ dosage of 1.67 g provides accurate results when chloride concentrations are below 1000 mg Cl^-/L, even at $HgSO_4$-to-chloride ratios below 10:1. The outcome reduces the chemical costs and hazardous waste, contributing to more sustainable laboratory practices. Higher chloride concentrations yielded elevated COD values due to chloride oxidation. The $HgSO_4$ dosage of 33.3 g effectively mitigated chloride interference up to 2000 mg Cl^-/L. Furthermore, a cooling time of 16 hours influenced COD titration when excess $HgSO_4$ precipitated and remained in the samples, creating cloudy $HgSO_4$ particles that interfered with endpoint detection. The findings reveal the effects of prolonged cooling time on COD measurements and contribute new information for improving COD analysis practices.

Keywords: COD analysis, Cooling time, Mercury sulfate, Mercury precipitates, Chloride oxidation

1.0 INTRODUCTION

Chemical Oxygen Demand (COD) is a standard method for indirectly quantifying the organic matter in water and wastewater. It determines the oxygen demand from chemical reactions between organic compounds, an oxidizing agent, a strong acid, and a catalyst at high temperatures, producing carbon dioxide and water as byproducts. Generally, open reflux and closed reflux are two methods available for COD measurements in water and wastewater samples; however, the closed reflux method has been widely used due to the much lower volume of COD chemical waste [1]. Significant attention has been given to the challenges posed by interferences in standard COD measurements. Some chemicals, including pyridine and volatile organic compounds, are reported as interferences for the COD analysis [1]. Peracetic acid (PAA) is a common disinfectant and oxidant in wastewater treatment, breaking down into hydrogen peroxide (H_2O_2), oxygen, water, and acetic acid [2-3]. PPA can interfere with the COD measurement by artificially increasing the COD values. It was found that 1 mg/L PPA can contribute to the COD concentration of 13.5 mg COD/L [4]. Furthermore, the strong oxidizing agent also oxidizes the inorganic compounds, such as the halide group in the samples, including bromide, chloride, and iodide, causing erroneous COD results. The halide group may also react with dichromate, producing elemental halogen and chromic ions rather than oxidizing organic materials [1]. Bromide in water samples seriously interferes with the COD analysis, resulting in a falsely high COD value [5]. Chloride is also a well-known interference in OD measurements because it can react with silver sulfate (Ag_2SO_4) catalyst to form silver chloride, precipitating subsequently out of the solution. The chemical reactions of COD analysis could not have been completed without silver being used as a catalyst. In addition, chloride can react with the dichromate reagent, called chloride oxidation, as shown in Equation 1. It shows that 6 moles of Cl^- require the equivalent of 3 moles of O_2 with the dichromate ion as an oxidizing agent, forming 3 moles of Cl_2. Converting this stoichiometric relationship to a mass basis gives a theoretical oxygen demand (ThOD) for chloride of 0.226 mg O_2 per mg of Cl^- [6, 7]. Thus, a theoretical COD of 226 mg/L is anticipated for a sample containing 1000 mg Cl^-/L, leading to inaccurate COD measurements.

$$6Cl^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Cl_2 + 2Cr^{3+} + 7H_2O \qquad (1)$$

The standard COD measurement has been reported to be inaccurate for samples with chloride concentrations exceeding 2000 mg Cl^-/L [1]. In cases where samples contain high concentrations of both organics and chloride, diluting the sample to reduce chloride concentration can prevent interference effects. However, the dilution cannot be used with high chloride but with a low concentration of organics in which COD also becomes more diluted, and chloride oxidation unavoidably occurs [8, 9]. According to the standard methods [1], mercuric sulfate ($HgSO_4$) is typically added to the dichromate solution at the $HgSO_4$:Cl^- weight ratio of 10:1 to adequately mask the chloride interference up to the chloride concentration of 2000 mg/L by precipitating chloride as $HgCl_2$. 33.3 g $HgSO_4$ was required for the standard method of COD analysis. It is suggested that greater concentrations of $HgSO_4$ with the constant weight ratio of $HgSO_4$:Cl^- hinder the chloride interference [1, 6] adequately. However, this $HgSO_4$:Cl^- weight ratio resulted in substantial errors when samples contained low and moderate COD concentrations. Besides, extra $HgSO_4$ addition raises another concern about COD waste, which is hazardous because it contains high mercury, chromium, and silver concentrations [10, 11].

Alternate methods for COD analysis have been explored to mitigate chloride interference [12], such as using manganese (III) as an oxidizing agent and silver nitrate as a chloride masking agent. While this mercury-free approach demonstrated reproducibility with a mean recovery rate of 88.7% within the COD range of 20-500 mg/L, it has not gained acceptance as a standard due to its relatively lower recovery rate than the dichromate method [13]. Similarly, electrochemical sensors have been proposed, but they face standardization and reproducibility challenges, making them less viable as replacements for traditional methods due to several drawbacks [14]. Several researchers studied and proposed several other methodologies, but they are not foolproof and have not yet been accepted as the standard method for the COD measurement. Nevertheless, the traditional method with dichromate as the oxidizing agent is still the most preferred and accepted as the standard COD analysis procedure.

The cooling time before titration, an often-overlooked factor, may influence the accuracy of COD measurements with the closed reflux methods. Although the Standard Methods [1] suggest that precipitated $HgSO_4$ does not affect analysis, prolonged cooling times might allow for significant precipitate formation or dissolution, potentially interfering with the titration process. In common laboratory practice, samples are often left to cool for periods ranging from a few hours to overnight (2-16 hours) before titration, resulting from various practical aspects such as batch processing of samples and scheduling constraints. Given the lack of studies exploring this variable, this research aims to fill that gap by systematically evaluating the effects of cooling time before titration on COD accuracy, particularly in the presence of varying $HgSO_4$ concentrations. Furthermore, because $HgSO_4$ is a toxic substance used to mask chloride interference in COD analysis, minimizing its concentration could reduce waste without compromising analytical accuracy. Therefore, the objectives of this study were to assess the combined impact of cooling time and mercury concentration on COD measurement accuracy while also exploring the feasibility of minimizing $HgSO_4$ dosage to decrease the generation of hazardous waste. In this study, experiments were conducted using a known COD concentration of a simple organic compound, allowing the detection of any systematic errors.

2.0 METHODOLOGY

2.1 Synthetic Water Sample Preparation

The experiments were conducted in the Environmental Engineering Laboratory of the Department of Chemical Engineering, Burapha University, Thailand. Six aliquots of water samples were prepared from a 10,000 mg/L dextrose stock solution, a simple sugar chemically identical to glucose. Each aliquot was adjusted to achieve a COD concentration of 300 mg COD/L. Chloride was added to the samples from a 100,000 mg Cl^-/L stock solution to achieve final chloride concentrations of 0, 500, 1000, 1500, 2000, and 2500 mg Cl^-/L in each aliquot. For chloride concentrations below 2000 mg Cl^-/L, the standard method recommends using 33.3 g of $HgSO_4$ to mask chloride interference completely. A chloride concentration of 2500 mg Cl^-/L was used to investigate the effects of exceeding 2000 mg Cl^-/L on COD measurements. Two different amounts of 1.67 and 33.3 g $HgSO_4$ were tested. A chloride-free aliquot was the control to evaluate the effects of varying $HgSO_4$ concentrations and cooling times on COD measurements. Initial COD and chloride concentrations were measured using closed reflux titrimetric and Argentometric methods, respectively [1]. Silver nitrate concentration of 0.0141 M was used as the titrant, while potassium chromate served as the indicator during the chloride determination in the solutions [1].

2.2 COD Experiments

The experiments followed the procedures listed in Table 1. To mask chloride interference, 1.67 g and 33.3 g of $HgSO_4$ were added to the standard potassium dichromate digestion solution. These two amounts were selected based on standard methods and stoichiometric considerations. The 33.3 g of $HgSO_4$ corresponds to the standard amount recommended by the APHA Standard Methods (5220C), which is designed to ensure complete masking of high chloride levels [1]. For this study, it was essential also to test a lower amount of $HgSO_4$ (1.67 g) to reflect more typical conditions in domestic wastewater, where chloride concentrations usually range from 30 to 90 mg/L [15], but may occasionally approach 1000 mg/L due to local factors such as infiltration of saline water, use of water softeners, and industrial contributions. The 1.67 g dose was calculated based on the stoichiometric ratio of $HgSO_4$:Cl^-, where each mole of $HgSO_4$ can complex with two moles of chloride. This results in an approximate $HgSO_4$:Cl^- weight ratio of 5.0:1, providing a sufficient excess of $HgSO_4$ to fully mask chloride in samples with up to 1000 mg Cl^-/L, while using significantly less $HgSO_4$ than the standard 33.3 g [1].

Table 1 Experimental design with different $HgSO_4$ masses, chloride concentrations, cooling times, and $HgSO_4$:Cl^- ratios

Run No.	$HgSO_4$, g	Chloride Concentration, mg Cl^-/L	Cooling Time, hrs	$HgSO_4$:Cl^- Weight Ratio
1	1.67	0	2, 4, 8, 16	-
2		500	2, 4, 8, 16	10.0:1
3		1000	2, 4, 8, 16	5.0:1
4		1500	2, 4, 8, 16	3.3:1
5		2000	2, 4, 8, 16	2.5:1
6		2500	2, 4, 8, 16	2.0:1
7	33.3	0	2, 4, 8, 16	-
8		500	2, 4, 8, 16	200:1
9		1000	2, 4, 8, 16	100:1
10		1500	2, 4, 8, 16	67:1
11		2000	2, 4, 8, 16	50:1
12		2500	2, 4, 8, 16	40:1

For sample dilution, 1 mL of synthetic water from each previously described aliquot was added to a 15 mL borosilicate culture tube (25 mm x 150 mm). Distilled water was added to each tube to bring the total volume to 5 mL, followed by adding 3.0 mL of standard potassium dichromate digestion solution containing 1.67 g of $HgSO_4$. Finally, 7.0 mL of sulfuric acid reagent, prepared using concentrated sulfuric acid and silver sulfate (Ag_2SO_4) as the catalyst, was added to each tube, bringing the final volume to 15 mL. After capping the tubes with TFE-lined screw caps, the samples were inverted several times to mix the solutions thoroughly and then placed in a preheated oven at 150 °C for two hours of reflux. After two hours, the samples were removed from the oven and allowed to cool at room temperature for 2, 4, 8, and 16 hours, respectively. At each cooling time, the samples were titrated with standard ferrous ammonium sulfate (FAS) to measure COD concentrations. The experiments were repeated using 33.3 g of $HgSO_4$. The $HgSO_4$:Cl^- weight ratios in Table 1 were calculated according to Equation 2.

$$HgSO_4 : Cl^- = \frac{(A)\cdot V_{dichromate}}{(B)\cdot V_{sample}} \tag{2}$$

Where A represents the concentration of $HgSO_4$ in mg/mL, corresponding to 1.67 mg/mL and 33.3 mg/mL when 1.67 g and 33.3 g of $HgSO_4$ were added to 1 L of the standard potassium dichromate digestion solution; B is the concentration of chloride in sample in mg/mL; $V_{dichromate}$ denotes the volume of the digestion solution (3 mL), and V_{sample} represents the sample volume in mL (1 mL).

2.3 Statistical Analysis

Experimental data are presented as mean ± standard deviation (SD). Statistical analysis was conducted using Minitab software with one-way analysis of variance (ANOVA). The Tukey pairwise comparison was selected for the ANOVA analysis. Statistically significant differences between factors, including $HgSO_4$ amounts and cooling times, were reported when the p-value was less than 0.05 ($p < 0.05$).

3.0 RESULTS AND DISCUSSION

3.1 COD and Chloride Concentrations of COD Samples

A known COD concentration of approximately 300 mg/L without chloride was prepared in a sample using dextrose and measured using the closed reflux titrimetric method, with 1.67 g and 33.3 g of $HgSO_4$ used as a chloride-masking agent and dichromate as the oxidizing agent. At the beginning of the experiments, a cooling period of 2 hours was allotted to allow the COD tubes to reach room temperature before titrating the samples with FAS. The measured average COD concentration in the samples was 260±35 mg/L for 1.67 g $HgSO_4$ and 280±20 mg/L for 33.3 g $HgSO_4$. It is reported that glucose's ThOD is 10.45 mg/L at a glucose concentration of 10 mg/L [16]. From the stoichiometric relationship between glucose and oxygen, it is known that 6 moles of O_2 are required to oxidize one mole of glucose, resulting in a ThOD for glucose of 1.067 mg O_2 per mg of glucose. The COD value of glucose obtained through the dichromate reflux method was approximately 97% of the ThOD value [17], resulting in an expected COD value of about 310 mg COD/L [(1.067 mg O_2 per mg of glucose) x (300 mg glucose/L) x 97%]. The COD values measured in this study were lower than the target concentration of 300 mg/L, possibly due to variability in chemical reagents and potential human errors during sample handling. However, a one-way ANOVA indicated no statistically significant difference between the 1.67 g and 33.3 g $HgSO_4$ concentrations during COD measurement at a 2-hour cooling period ($p > 0.05$). This suggests that while procedural and reagent-based variability may contribute to minor discrepancies, the differences are within the expected experimental variation and are not statistically significant. Therefore, it can be concluded that the $HgSO_4$ amount did not significantly affect the COD concentrations in these tests, suggesting that $HgSO_4$ is unnecessary in the absence of chlorides because the two sets of sample aliquots showed statistical similarity. The results of this study on the effect of varying $HgSO_4$ concentrations in COD measurement align closely with the findings of Almutairi [18]. In samples without significant chloride levels, the study found that Hg-free COD vials achieved results comparable to traditional Hg-based methods, reinforcing the conclusion that $HgSO_4$ may not significantly impact COD values under these conditions. This supports our observation that variations in $HgSO_4$ did not yield statistically different COD values in chloride-free samples, suggesting that $HgSO_4$ could be minimized or omitted in such tests.

3.2 Effects of Different $HgSO_4$ Concentrations at Various Chloride Levels

Experiments were conducted to measure the COD of samples with varying chloride concentrations (0, 500, 1000, 1500, 2000, and 2500 mg Cl^-/L) using two different quantities of $HgSO_4$ (1.67 g and 33.3 g). After preparation, the samples were allowed to cool for 2 hours. Statistical analysis revealed significant differences in COD measurements among the two $HgSO_4$ dosages of 1.67 g and 33.3 g and across the various chloride concentrations ($p < 0.05$). As shown in Figure 1, when 33.3 g of $HgSO_4$ was used, following the Standard Methods for the Examination of Water and Wastewater [1], the COD concentrations remained consistent, averaging 296.7±40.7 mg COD/L, suggesting that chloride interference was effectively masked, as indicated by the horizontal orange dashed trend line in Figure 1. Furthermore, the R^2 value of 0.2246 indicates a weak correlation, suggesting that the increasing chloride concentration had little to no impact on COD results. A one-way ANOVA confirmed no statistically significant difference in COD values across different chloride concentrations when 33.3 g of $HgSO_4$ was used. The reason is that $HgSO_4$ complexes with chloride ions under strongly acidic conditions and high chloride concentrations to form mercury chloride precipitates and mercury chloride complexes, including $[HgCl_3]^-$ and $[HgCl_4]^{2-}$ [19], preventing their oxidation by dichromate reagents into free chlorine, which would otherwise inflate COD values. Interestingly, these results suggest that chloride interference at concentrations exceeding 2000 mg Cl^-/L can be effectively masked with sufficient $HgSO_4$ of 33.3 g, resulting in stable COD measurements. This observation extends the applicability of the COD test beyond the APHA recommendation [1], provided that appropriate measures are employed. For example, it was reported that a $HgSO_4$:Cl^- weight ratio of 20:1 achieved less than 10% error in samples containing up to 40 g NaCl/L and low COD concentrations (20-230 mg COD/L) [20]. On the other hand, when only 1.67 g of $HgSO_4$ was used, a statistically significant difference in COD values was observed ($p < 0.05$), as listed in Table 2, indicating inadequate masking of chloride interferences. Notably, COD results increased with chloride concentrations exceeding 1000 mg/L due to the contribution of chloride to overall COD measurements by chloride oxidation and chloride interferences [1, 9, 19]. This finding aligns with the ThOD for chloride of 0.226 mg O_2 per mg of Cl^-. In such cases, residual chloride can react with dichromate to produce chlorine and chromic ions, as shown in Equation 1, leading to a positive error with higher COD readings.

Table 2 Statistical results from the one-way ANOVA analysis at two $HgSO_4$ dosages and different chloride concentrations

Source	DF	Adj. SS	Adj. MS	F-value	p-value
$HgSO_4$	1	653403	653403	42.80	0.0000000010
Error	142	2167861	15267		
Total	143	2821264			

Remark: DF = total degrees of freedom; Adj.SS = adjusted sums of squares; Adj. MS = adjusted mean squares

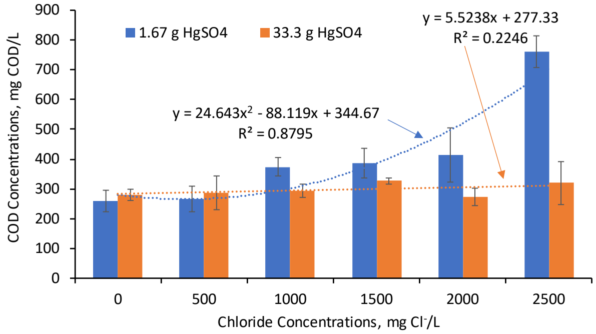


Figure 1 COD concentrations (mean ± SD, mg COD/L) for samples containing varying chloride concentrations (0-2500 mg Cl^-/L), measured after 2 hours of cooling time using the standard dichromate method with two $HgSO_4$ dosages (1.67 g and 33.3 g) as chloride masking agents.

According to the COD procedure [1] and Kayaalp et al. [9], an $HgSO_4$:Cl^- weight ratio of 10:1 is recommended. The $HgSO_4$:Cl^- weight ratios used in this experiment were 200:1, 100:1, 67:1, 50:1, and 40:1 at chloride concentrations of 500, 1000, 1500, 2000, and 2500 mg Cl^-/L, respectively, when 33.3 g of $HgSO_4$ was added to the dichromate reagent. Conversely, COD concentrations increased with chloride levels above 1000 mg Cl^-/L when only 1.67 g of $HgSO_4$ was used, indicating that this lower $HgSO_4$ amount was insufficient to fully mask chloride interferences. The corresponding $HgSO_4$:Cl^- weight ratios were 10:1, 5:1, 3.3:1, 2.5:1, and 2:1 at chloride concentrations of 500, 1000, 1500, 2000, and 2500 mg Cl^-/L, respectively. However, 1.67 g of $HgSO_4$ did appear sufficient to suppress chloride interference at chloride concentrations below 1000 mg Cl^-/L, suggesting that reducing $HgSO_4$ dosage from 33.3 g to 1.67 g could minimize the ecological footprint and environmental impact and reduce the operational costs associated with disposing of hazardous materials. Nevertheless, the experimental results indicate that this reduction is only viable for chloride-free or low-chloride samples. If this limit is exceeded, measurements of COD display significant positive COD errors, compromising the reliability of the COD analysis.

3.3 Effects of Cooling Time on COD Concentrations at Different Chloride Levels

The effects of cooling times before COD titration (2, 4, 8, and 16 hours) were evaluated at varying chloride concentrations (0, 500, 1000, 1500, 2000, and 2500 mg Cl^-/L) and different $HgSO_4$ dosages (1.67 g and 33.3 g), as shown in Figures 2 and 3, respectively. As shown in Figure 2, cooling time did not significantly affect COD measurements for samples without chloride when 1.67 g of $HgSO_4$ was used in the digesting solution. The average COD concentration determined with 1.67 g of $HgSO_4$ was 287±25 mg COD/L. The absence of chloride or its low concentration (< 1000 mg Cl^-/L) minimizes the interference from chloride ions, making the COD results stable regardless of cooling duration. However, when the samples contained chloride concentrations above 1000 mg Cl^-/L, 1.67 g of $HgSO_4$ was insufficient to precipitate all chloride, resulting in higher COD concentrations due to the chloride oxidation [9, 21], as previously discussed. Statistical analysis using one-way ANOVA revealed no statistically significant difference between cooling times for COD measurements. Notably, a cooling time of 16 hours led to a dramatic increase in COD concentration to approximately 633 mg COD/L at a chloride concentration of 2000 mg Cl^-/L. It is possible that some AgCl precipitates (K_{sp} at 25 °C is 1.77 x 10^{-10} [22]) can form soluble silver-chloride complexes such as $[AgCl_2]^-$ (K_f at 25 °C is 1.1 x 10^5 [22]) under high chloride concentrations [23]. The formation constant (K_f) indicates that $[AgCl_2]^-$ can significantly increase the solubility of AgCl under high chloride concentrations. It is evident from the white precipitates, as shown in Figure 4(a), found in the COD tubes when the chloride concentrations were 1500, 2000, and 2500 mg Cl^-/L at the $HgSO_4$:Cl^- weight ratios of 3.3:1, 2.5:1, and 2:1, respectively. The white precipitates disappeared from the solutions at 16 hours of cooling time at the chloride concentration of 2000 mg Cl^-/L. However, it is known that neither mercury-chloride nor silver-chloride complexes can react with the dichromate reagent to oxidize chloride because they do not exist as free chloride ions. Therefore, it is reasonable to assume that higher COD values at the prolonged cooling time are most likely caused by the slow and continued oxidation of un-complexed chlorides with the dichromate reagent, contributing to the elevated COD values. Furthermore, the COD concentrations remained consistently high across all cooling times at a 2500 mg Cl^-/L chloride concentration, suggesting that the solutions were saturated with chloride interferences, thereby limiting the availability of dichromate, which could not oxidize the unmasked chloride.

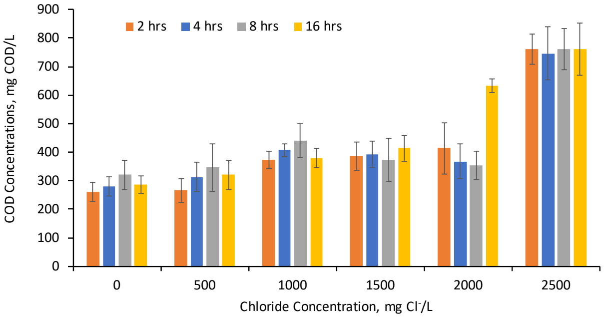


Figure 2 COD concentrations (mean ± SD, mg COD/L) for samples with varying chloride concentrations (0-2500 mg Cl^-/L), measured using 1.67 g $HgSO_4$ after 2, 4, 8, and 16 hours of cooling time.

Figure 3 illustrates COD concentrations at different cooling times (2, 4, 6, 8, and 16 hours) with an $HgSO_4$ dosage of 33.3 g, following APHA procedures [1]. Generally, the COD concentrations measured at different chloride levels remained consistent across the cooling times, with average COD concentrations of 288±6, 285±11, 285±17, 307±20, 283±26, and 332±48 mg COD/L at chloride concentrations of 0, 500, 1000, 1500, 2000, and 2500 mg Cl^-/L, respectively. All samples were clear with a yellowish tint, and no AgCl particles were observed after the chemicals were added, suggesting that mercury reacted with chloride to form $HgCl_2$. However, visual observations revealed precipitates in the COD tubes, as shown in Figure 4(b), after different cooling times. The precipitates appeared at the cooling times of 4, 8, and 16 hours when the samples contained no chloride. It is possible that excess $HgSO_4$ contributed to the formation of precipitates over time. When the chloride concentrations increased from 500, 1000, 1500, and 2000 mg Cl^-/L, the precipitates were found at the cooling times of 8 and 16 hours. These precipitates are attributed to the formation of $HgCl_2$ as chloride reacts with $HgSO_4$ under prolonged cooling, exceeding the solubility limit of $HgCl_2$. It appears that the standard deviation of COD concentrations at a chloride level of 2500 mg Cl^-/L was greater than that of other samples because the COD value determined after 16 hours of cooling increased to 400 mg COD/L. Errors in COD measurement occurred because the solutions contained particles, and the titration endpoint colors were unclear, complicating endpoint determination. Observations suggest that the extended cooling time of 16 hours increased the formation of additional precipitates, possibly due to temperature fluctuation over time [1]. It is noted that the $HgSO_4$:Cl^- weight ratio in this experiment was 40:1. These findings suggest that both $HgCl_2$ and excess $HgSO_4$ precipitates could interfere with COD analysis in this study. These results contradict the APHA, which states that $HgSO_4$ precipitates do not affect COD analysis, suggesting the need for further investigations to evaluate the impact of $HgSO_4$ precipitates on COD accuracy.

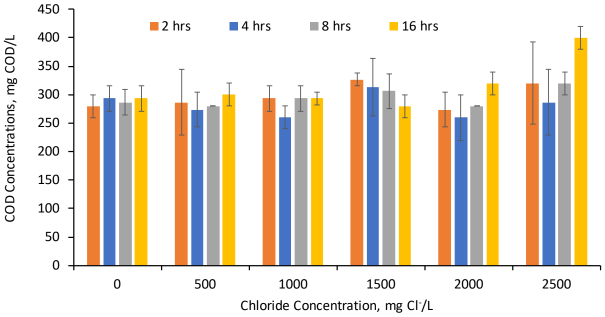


Figure 3 COD concentrations (mean ± SD, mg COD/L) for samples with varying chloride concentrations (0-2500 mg Cl^-/L), measured using 33.3 g $HgSO_4$ after 2, 4, 8, and 16 hours of cooling time.

Figure 4 Precipitates were observed in the tube with (a) 1.67 g of $HgSO_4$ and (b) 33.3 g of $HgSO_4$

4.0 CONCLUSION

It is shown from the experimental results demonstrate that using 1.67 g of $HgSO_4$ could mask the chloride interferences completely at the chloride concentration below 1000 mg Cl-/L to provide accurate COD measurements, even though the $HgSO_4$:Cl^- weight ratio is less than 10:1. This finding indicates that a lower $HgSO_4$ dosage at the $HgSO_4$:Cl^- weight ratio less than 10:1 can be efficiently applied to low-chloride samples, which helps lower chemical expenses and minimize hazardous waste production, thereby promoting more sustainable laboratory practices. However, at higher chloride concentrations, this amount of mercury sulfate is insufficient to eliminate all chloride, leading to elevated COD values due to the oxidation of dichromate by unmasked chloride ions. Additionally, more white precipitates formed at higher chloride concentrations, causing errors in endpoint determination during FAS titration. Nevertheless, it is suggested that cross-validation with alternative methods to quantify residual chloride and organic content and assess different sample types should be conducted to ensure the accuracy and reliability of this approach at low $HgSO_4$ dosages. Increasing the $HgSO_4$ amount to 33.3 g effectively masks chloride interference up to 2000 mg Cl^-/L, as recommended by the Standard Methods for the Examination of Water and Wastewater, with the $HgSO_4$:Cl^- weight ratio greater than 10:1. However, the experiments revealed that prolonged cooling time can negatively impact COD analysis by allowing the formation of excess $HgSO_4$ precipitates at a cooling time of 16 hours, possibly due to temperature fluctuations or extended interactions between excess $HgSO_4$ and the sample matrix. These cloudy particles interfered with the accurate determination of endpoints during titration, highlighting a limitation of this study. Additionally, future research should focus on optimizing sample handling protocols, exploring alternative titration endpoint methods, and conducting validation studies with different types of samples.

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Conflicts of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper

References

[1] APHA, AWWA and WEF. 2023. *Standard Methods for the Examination of Water and Wastewater*. 24th ed. Washington DC: American Public Health Association. DOI: 10.2105/SMWW.2882.103

[2] Ao, X. W., Eloranta, J., Huang, C. H., Santoro, D., Sun, W. J., Lu, Z. D. and Li, C. 2021. Peracetic Acid-based Advanced Oxidation Processes for Decontamination and Disinfection of Water: A Review. *Water Research*. 188: 116479. DOI: https://doi.org/10.1016/j.watres.2020.116479.

[3] Kim, J. and Huang, C. H. 2021. Reactivity of Peracetic Acid with Organic Compounds: A Critical Review. *ACS ES&T Water*. 1(1):15-33. DOI : https://doi.org/10.1021/acsestwater.0c00029

[4] Leite, L. S., Tango, M. D., Filho, J. A. Z, Hoffmann, M. T. and Daniel, L. A. 2021. Implications of COD Analysis Use in the Peracetic Acid-based Wastewater Treatment. *Water Science & Technology*. 84(5): 1270-1279. DOI: https://doi.org/10.2166/wst.2021.300

[5] Shi, X., Huang, S., Yeap, T. S., Ong, S. L. and Ng, H. Y. 2020. A Method to Eliminate Bromide Interference on Standard COD Test for Bromide-rich Industrial Wastewater. *Chemosphere*. 240: 124804. DOI: https://doi.org/10.1016/j.chemosphere.2019.124804

[6] Canelli, E., Mitchell, D. G. and Pause, R. W. 1976. An Improved Determination of Chemical Oxygen Demand in Water and Wastes by a Simplified Acid Dichromate Digestion. *Water Research*. 10(4):351-355. DOI : https://doi.org/10.1016/0043-1354(76)90179-2.

[7] Dobbs, R. A. and Williams, R. T. 1963. Elimination of Chloride Interference in the Chemical Oxygen Demand Test. *Analytical Chemistry*. 35(8): 1064:1067. DOI: https://doi.org/10.1021/ac60201a043

[8] Freire, D. D. C. and Sant'Anna, G. L. 1998. A Proposed Method Modification for the Determination of COD in Saline Waters. *Environmental Technology*. 19(12):1243-1247. DOI: https://doi.org/10.1080/09593331908616784.

[9] Kayaalp, N., Ersahin, M. E., Ozgun, H., Koyuncu, I. and Kinaci, C. 2010. A New Approach for Chemical Oxygen Demand (COD) Measurement at High Salinity and Low Organic Matter Samples. *Environmental Science and Pollution Research*. 7: 1547-1552. DOI: https://doi.org/10.1007/s11356-010-0341-z.

[10] Sousa, A.C., Lucio, M. M. L, Neto, O. F. B., Marcone, G. P., Pereira, A. F., Dantas, E. O., Fragoso, W. D., Araujo, M. C. U. and Galvão, R. K. H. 2007. A Method for Determination of COD in a Domestic Wastewater Treatment Plant by Using Near-infrared Reflectance Spectrometry of Seston. *Analytica Chimica Acta*. 588(2):231-236. DOI: https://doi.org/10.1016/j.aca.2007.02.022

[11] Dubber, D. and Gray, N.F. 2010. Replacement of Chemical Oxygen Demand (COD) with Total Organic Carbon (TOC) for Monitoring Wastewater Treatment Performance to Minimize Disposal of Toxic Analytical Waste. *Journal of Environmental Science and Health Part A*. 45(12): 1595-1600. DOI: https://doi.org/10.1080/10934529.2010.506116

[12] Aguilar-Torrejón, J. A., Balderas-Hernández, P, Roa-Morales, G., Eduardo Barrera-Díaz, C., Rodríguez-Torres, I. and Torres-Blancas, T. 2023. Relationship, Importance, and Development of Analytical Techniques: COD, BOD, and, TOC in Water-An Overview Through Time. *SN Applied Sciences*. 5: 118. DOI: https://doi.org/10.1007/s42452-023-05318-7

[13] Kolb, M., Bahadir, M. and 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: https://doi.org/10.1016/j.watres.2017.06.034

[14] Latif, U. and Dickert, F. L. 2015. Chemical Oxygen Demand. In: Moretto, L., Kalcher, K., editors. *Environmental Analysis by Electrochemical Sensors and Biosensors*. Nanostructure Science and Technology. New York: Springer. 719-728. DOI: https://doi.org/10.1007/978-1-4939-1301-5_1.

[15] Tchobanoglous, G., Burton, F. L. and Stensel, H. D. 2003. *Wastewater Engineering: Treatment and Reuse*. 4th ed. Boston:McGraw-Hill.

[16] Kim, Y. C., Sasaki, S., Yano, K., Ikebukuro, K., Hashimoto, K. and Karube, I. 2000. Relationship Between Theoretical Oxygen Demand and Photocatalytic Chemical Oxygen Demand for Specific Classes of Organic Chemicals. *Analyst*. 125(11): 1915-1918. DOI: https://doi.org/10.1039/B007005J

[17] Dedkov, Y. M., Elizarova, O. V. and Kel'ina, S. Y. 2000. Dichromate Method for the Determination of Chemical Oxygen Demand. *Journal of Analytical Chemistry*. 55: 777-781. DOI: https://doi.org/10.1007/BF02757915.

[18] Almutairi, M. S. 2021. Correlation of the Chemical Oxygen Demand of Water Using Hg and Hg-free COD Vials. *Journal of Water Chemistry and Technology*. 43: 401-406. DOI: https://doi.org/10.3103/S1063455X21050027.

[19] Hahne, H. C. H. and Kroontje, W. 1973. The Simultaneous Effect of pH and Chloride Concentrations Upon Mercury (II) as a Pollutant. *Soil Science Society of America Journal*. 37(6): 813-1000. DOI: https://doi.org/10.2136/sssaj1973.03615995003700060016x.

[20] Vyrides, I. and Stuckey, D. C. 2009. A Modified Method for the Determination of Chemical Oxygen Demand (COD) for Samples with High Salinity and Low Organics. *Bioresource Technology*. 100(2):979-982. DOI: https://doi.org/10.1016/j.biortech.2008.06.038.

[21] Zhao, Y., Tang, H., Ge, X., Li, Y. and Wang, S. 2021. The Chloride Ion to the Chemical Oxygen Demand (COD) Analysis of the Influence of Different Analysis Method. *E3S Web of Conferences*. 236:02034. DOI: https://doi.org/10.1051/e3sconf/202123602034.

[22] Averill, B. A. 2012. Solubility and Complexation Equilibriums. In: Averill, B. A., editors. *Principles of General Chemistry*. 2103-2104. Retrieved January 20, 2025, from https://2012books.lardbucket.org/.

[23] Fritz. J. J. 1985. Thermodynamic Properties of Chloro-complexes of Silver Chloride in Aqueous Solution. *Journal of Solution Chemistry*. 14: 865: 879. DOI: https://doi.org/10.1007/BF00646296.