

Comparison of COD Determination Methods FAS Titrimetric with UV-Vis Spectrophotometry

Intan Wulandari^{a)}, Uswatun Hasanah^{a*)}, and Siti Warnasih^{a)}

^{a)} Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Pakuan, Bogor 16163, Indonesia

^{*)} Corresponding Author: uswatun.hasanah@unpak.ac.id

Article history: received: 30-05-2023; revised: 05-06-2023; accepted: 06-09-2023; published: 06-09-2023.

ABSTRACT

Liquid waste is one of the factors causing contamination of the aquatic environment. One of the chemical parameters of water quality namely *Chemical Oxygen Demand* (COD). This research was conducted at three different concentration levels, namely low, medium, and high, with samples of river water, domestic wastewater, and sago liquid waste. The method used is UV-Vis spectrophotometry (SNI 6989.2: 2019) and FAS titrimetry (APHA, 2017 methods 5220 D); for the UV-Vis spectrophotometry method in the range < 90 mg/L, the wavelength was measured at 420 nm, while for high levels in the range 100 mg/L $< x < 900$ mg/L, it was measured at 600 nm. The quality control parameters used are accuracy and precision parameters. The purpose of this study was to compare the COD determination between UV-vis spectrophotometry and FAS titrimetry and to determine the validity and correlation of the two methods—a comparison of the results of the two methods used in the F test. The results showed that the COD values from UV visible spectrophotometry and FAS titrimetry yielded good precision and accuracy values and met the acceptable limits, namely %RSD $< 10\%$ and 90% accuracy $< \%R < 110\%$. However, the results of the COD analysis using the UV-Vis spectrophotometry method were lower by 0.8556 than the results of the COD analysis using the FAS titration method, with a correlation coefficient $r^2 = 0.982$. The average concentration of UV-Vis spectrophotometry in samples of sago wastewater was 572.141 mg/L, domestic wastewater was 113.525 mg/L, and river water was 42.98 mg/L. The average COD level of the titrimetric method in sago wastewater was 641.888 mg/L, domestic wastewater was 219.251 mg/L, and river water was 58.016 mg/L. The results of the F test for these two methods produce an $F_{\text{count}} > F_{\text{table}}$. The null hypothesis (H_0) is rejected, meaning there is a significant difference between the two methods.

Keywords: Chemical Oxygen Demand (COD), Uv-Vis Spectrophotometry, FAS Titrimetry, Method Validation, and Verification

1. INTRODUCTION

Water pollution occurs due to the disposal of residues from human business/activities on an industrial and domestic scale whose quality standards exceed acceptable limits. Wastewater can harm human life, animals, and the surrounding environment [1]. As a result of the presence of waste pollution, both industrial and domestic, will have an impact on health, damage the aesthetics of the environment, affect the quality of groundwater, and also have an effect on the life of aquatic biota, for example, decreasing levels of dissolved oxygen in the water so that it disrupts the need for oxygen in the water and inhibits growth.

Chemical parameters that can be measured in determining water quality are pH, TSS, BOD, and COD. However, in this study, the test will be carried out specifically on the COD parameter only, bearing in mind that the COD parameter is also essential in determining water quality [2] and is an indicator of water pollution. COD (Chemical Oxygen Demand) is total oxygen used to oxidize organic compounds contained in water chemically. Water that has a high COD content indicates that the pollutant content is also high, so this can lead to the poor oxygen content in water bodies, which will then the problem of environmental pollution today requires a quick, effective, and efficient settlement method so that the issue of environmental pollution can be resolved

correctly and on target. Various methods can be used to determine COD levels, either classically or classically modern. This study used the closed reflux method using uv-vis spectrophotometry (SNI 6989.2: 2019) and the secure reflux method using titrimetry (APHA, 2017 methods 5220 D). A comparison of the two methods is needed so a laboratory can plan the method to be used appropriately before the test. Testing will be performed on ranges of *high range* and *low range*. The three samples that will be used in this test are samples of sago liquid waste taken from sago artisans in the Sogiri Prince area, Ciliwung river water samples in the Pondok Rajeg area, and samples of domestic liquid waste taken from residential waste disposal in the Cicadas area.

An important question related to the two methods is whether the two methods have equally valid performance and whether the two methods can be substituted for each other. If the two methods can replace each other (same performance), is it applicable for all concentration levels, both low ($\text{COD} < 100 \text{ mgO}_2/\text{L}$) as well as high ($100 \text{ mgO}_2/\text{L} < \text{COD} < 1000 \text{ mgO}_2/\text{L}$). For this reason, a test laboratory must ensure that the test method used is the latest edition. The test method must be validated and verified in advance to ensure that the test method can be accounted for its correctness and accuracy. This study aims to compare the validation and verification values of the two test methods to determine whether the two methods can be appropriately implemented in the testing laboratory. Verification can guarantee the results obtained from a measurement so that objective and reliable data is received [3]. Quality control parameters used in this study are accuracy and precision. The results of this study will be tested through a statistical test, namely the F test.

2. METHODS

Sample preservation (APHA, 2017 methods 5220 D and SNI 6989.2: 2019), If not used immediately, the test sample is preserved by adding H_2SO_4 concentrated to $\text{pH} < 2$ and stored in a cooler at $4 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ with a maximum recommended storage time of 7 days. Preparation of reagents (APHA, 2017 methods 5220 D) and SNI 6989.2: 2019)

2.1. Preparation of a standard solution of Potassium Hydrogen Phthalate (KHP) is equivalent to a COD value of 500 $\text{mg O}_2/\text{l}$ (SNI, 6989.2:2019 and (APHA, 2017 methods 5220 D).

Gently grind the KHP crystals, then dry them in the oven at 110°C until the weight remains. Dissolve 425 mg of KHP in organic-free water, adjust to 1,000 ml, and then homogenize.

2.2. Preparation of digestion solutions for reflux SNI, 6989.2:2019)

Digestion solution for high concentrations: added 10.216 g $\text{K}_2\text{Cr}_2\text{O}_7$, which was baked at 150°C for 2 hours into 500 mL of water. Then the addition of 167 mL H_2SO_4 was concentrated gradually (keeping hot) and 33.3 g HgSO_4 , dissolved and cooled to room temperature, and diluted to 1000 mL. Digestion solution for low concentrations:

Added 1.0216 g $\text{K}_2\text{Cr}_2\text{O}_7$, baked at 150 for 2 hours into 500 mL of water. Then the addition of 167 mL H_2SO_4 was concentrated little by little (keeping hot), and 33.3 g HgSO_4 was dissolved and cooled to room temperature and diluted to 1000 mL.

2.3. Preparation of 0.1 N FAS solution (APHA, 2017 methods 5220 D).

Added 39.2 g $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 500 mL of distilled water, then 20 mL of H_2SO_4 concentrate little by little (keep the heat), cooled, and added distilled water up to 1000 mL.

2.4. Preparation of 0.1 N dichromate standard solution (APHA, 2017 methods 5220 D).

$\text{K}_2\text{Cr}_2\text{O}_7$ primary standard was dissolved $\text{K}_2\text{Cr}_2\text{O}_7$ 4.903 g, which was baked at 150°C for 2 hours, then add 167 ml H_2SO_4 and 33.3 g HgSO_4 , then diluted with distilled water up to 1000 mL.

2.5. Preparation of titration indicator ferroin solution (APHA, 2017 methods 5220 D).

Added 1.485 g 1,10-phenanthroline monohydrate together with 695 mg $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water to 100 ml.

The tools used in this study include a Digestion vessel (16mm x 100 mm), COD reactor (Heating Block), pH meter, oven, measuring flask, volume pipette (5 ml, 15 ml, 20 ml, 25 ml), measuring pipette (5 ml, 10 ml, 15 ml), Erlenmeyer, beaker, magnetic stirrer, measuring pipette 5ml, 10ml, 15ml), micropipette, burette, scale analytical, visible spectrophotometer, and cuvette. The materials used in this study include H₂SO₄, K₂Cr₂O₇, HgSO₄, Ag powder₂SO₄, NH₂SO₃H (Sulfamic Acid), demineralized water, digestion solution, and potassium hydrogen phthalate solution.

3. RESULTS AND DISCUSSION

Procurement of Research Materials used is sago liquid waste taken from sago artisans in the Sogiri area, domestic waste taken from housing BTN Cicadas Permai Gunung Putri, and Ciliwung river water from the Pondok Rajeg area.

3.1. COD Determination Results

Standardization of 0.1 N FAS Solution are using (NH₄)₂Fe(SO₄)₂. FAS is used as a titrant to titrate excess potassium dichromate.

Table 1. Test results for the determination of COD by the Titrimetric Method individually and on average if the procedure is performed repeatedly.

Repetition	Sample		
	Sago (mg/L)	Domestic (mg/L)	river (mg/L)
1	643.507	218.892	59.584
2	643.507	219.520	56.448
3	639.744	219.520	56.448
4	639.744	218.892	58.016
5	643.507	219.520	58.016
6	643.507	219.520	59.584
7	639.744	218.892	58.016
Average	641.894	219.251	58.016
SD	2.01	0.33	1.280
%RSD	0.31	0.15	2.20
CV Horwitz	6.04	7.11	8.68
%RSD < CV repeatability	3.02	3.50	4.34
	Acceptance		
%RSD < CV repeatability	0.31 <	0.15 <	2.20 <
	3.02	3.50	4.34

The precision value obtained is included in the acceptability value by fulfilling the requirements

for % RSD < 10 % and % RSD < CV repeatability. The COD determination results from the UV-Vis spectrophotometric method Linearity Test Results UV-Vis Spectrophotometry Method. Variations in the concentration of standard solutions made by researchers for low concentrations are 10 mg/L, 30 mg/L, 50 mg/L, 70 mg/L, and 90 mg/L. For high and moderate levels, the concentration variations were 100 mg/L, 300 mg/L, 500 mg/L, 700 mg/L, and 900 mg/L.

The range of methods expressed by the lowest and highest concentrations of analytes in which the analytical method provides the accuracy, precision, and accepted linearity as parameters for the existence of a linear relationship is used.

From the average measured concentration, the higher the sample concentration measured, the smaller the % RSD produced, so the precision value obtained is good. Correlation coefficient (r) in linear regression $y = bx \pm a$. An ideal linear relationship is achieved if the values $b = 0$ and $r = +1$ or -1 , depending on the direction of the line. The sensitivity of the analysis, especially the instruments used, is indicated by the value of an intercept [4]. The best linearity is evaluated and observed on the plot, which states the relationship between analyte concentration and absorbance [5]. The measurement results of standard solutions using UV-Vis spectrophotometry instruments (**Figure 1**).

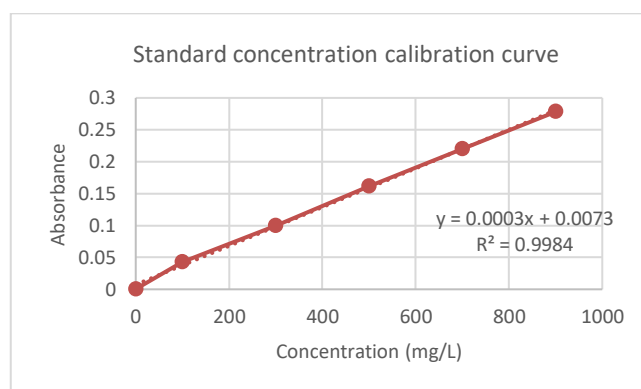


Figure 1. High standard solution calibration curve

Figure 1 shows testing on the high concentration range, which is based on chromium (III) measurement from the reduction of potassium dichromate by organic compounds in the test sample [6]. Based on the calculation of the linearity value, the regression equation is $Y=0,0003x +0,0073$, and the correlation coefficient value is 0.9984. The higher the

standard solution concentration, the greater the readable absorbance value. This is due to the formation of Cr^{3+} [7]. This shows a linear relationship between concentration and absorbance in measurements with the UV-Vis spectrophotometry method using a wavelength of 600 nm.

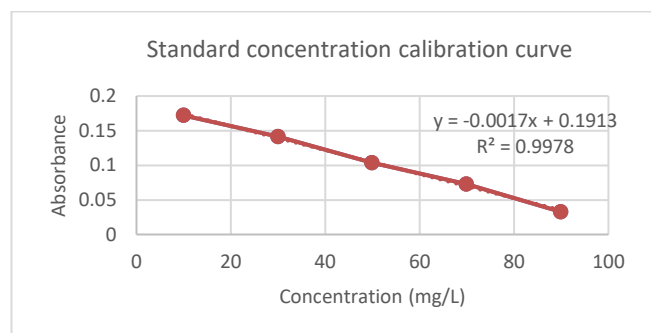


Figure 2. Low standard solution calibration curve

Figure 2 shows the test results in the low concentration range based on chromium (VI) measurement from the rest of the potassium dichromate used in the oxidation reaction of organic compounds [6]. Measurements were made at a wavelength of 420 nm, and the occurrence of the inverse ratio between standard concentration and absorbance so that the resulting curve decreases. The equation value is $y = -0.0017x + 0.1913$, and the correlation coefficient value (R^2) is obtained by 0.9978.

Table 2. Test results for the determination of COD by the Titrimetric Method individually

Repetition	Sample		
	Sago (mg/L)	Domestic (mg/L)	river (mg/L)
1	575.67	113.67	43.17
2	572.33	114.00	42.88
3	573.33	114.33	43.41
4	573.33	113.67	42.47
5	567.33	113.67	43.41
6	575.67	112.67	43.52
7	567.33	112.67	42.00
Average	572.141	113.525	42.98
SD	3.51	0.63	0.56
% RSD	0.61	0.55	0.013
CV Horwitz	6.15	7.84	9.08
CV Repeatability	3.07	3.92	4.54
Acceptance			
% RSD < CV	0.61 < 3.07	0.55 < 3.92	0.013 < 4.54
Repeatability			

Reacquisition (recovery) with the addition of 10% analyte. the average obtained for river samples. domestic samples. and samples of sago liquid waste can be seen in the **Table 2** [8]. The results showed

that the sample was in the acceptability range of 97% - 103% [4]. There is a % recovery which is more than 100% or the accuracy test results of the UV-Vis spectrophotometric method the measurement result is greater than the actual concentration. This is due to the uncertainty in calibration. both in the tools use and in the scales reading. or because the temperature affects the calibration. causing standard uncertainty [9]. The accuracy values obtained from the three samples tested are shown in **Table 3**.

Table 3. The result of the Uv-Vis Spectrophotometric Methode Accuracy Test

Repetition	% Recovery		
	Waste sago liquid (%)	Waste domestic (%)	river (%)
1	97.89	96.72	96.85
2	96.29	97.07	98.47
3	96.26	96.27	96.94
4	96.26	96.72	99.93
5	96.13	96.72	96.94
6	97.98	98.15	100.62
7	96.13	98.15	96.97
Acceptance limit = 97% < R < 103% [4]			

In the accuracy test, the results were as shown in the table above, so it was concluded that the UV-Vis spectrophotometry method has a good accuracy value and is included in the acceptance range, namely in the 97% - 103%

3.2. The relationship between the two methods

The F test result for domestic waste comparison is $F_{count} = 0,2811$ and $F_{table} = 0.2334$. Then test $F_{count} > F_{table}$ so that the result of the comparison of the two methods can be obtained, namely that H_0 rejected, it shows that there is a marked difference between the two methods [10]. The result of the F test for comparison of river samples for the F comparison test is $F_{count} = 5.1008$. $F_{table} = 4.2838$. Then test $F_{count} > F_{table}$, so it is concluded that H_0 is rejected. It shows that there is a marked difference between the two methods (**Figure 3**).

The COD analysis results of the UV Vis (Y) spectrophotometric method were 0.8556 lower than the COD analysis results of the FAS Titration method. The difference in the concentration of chemical oxygen demand between the two methods can be caused by differences in the treatment of the samples to be tested, the less maximal reaction that occurs during sample preparation, reduced purity of the

material used to be measured by the Uv-Vis spectrophotometry method [11]. The systematic error factor is due to the presence of other substances that affect the measurement results. This can cause the results to be smaller or larger than they should be.

In the law Lambert-beer, there is an absolute deviation. This can be caused by the concentration of the solution being too concentrated or too low. Several things can cause deviations in the law Lambert-beer [12]. Among them are chemical factors, namely ionization, and hydrolysis, which can cause the reaction concentration of a particle with water to decrease, and instrumental deviations always cause negative absorbance errors. The COD determination of the titrimetric method is greater than the UV-Vis spectrophotometric method.

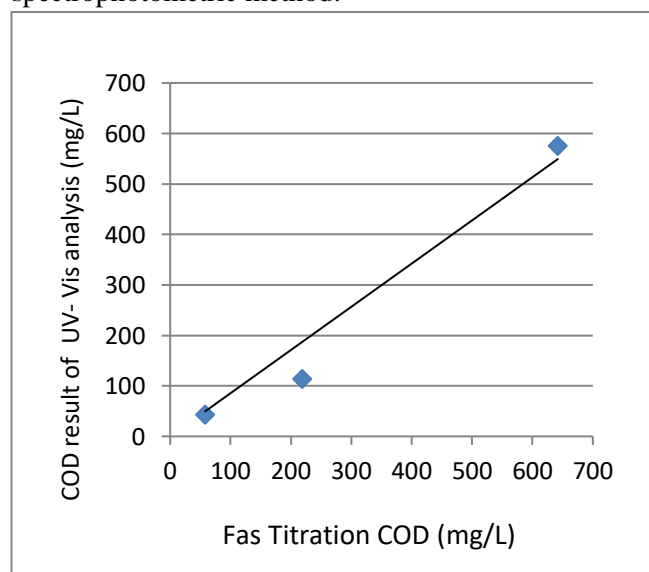


Figure 3. Correlation graph of the results of the COD analysis method FAS Titration with UV-Vis spectrophotometry method

4. CONCLUSION

Based on the research that has been done, it can be concluded that from the tests of the three wastes above, it is concluded that $F_{count} > F_{table}$ so that the UV-vis spectrophotometry method (SNI 6989.2: 2019) and FAS titrimetry (APHA, 2017 methods 5220 D) has a significant difference between both at low and high concentration levels. Both test methods have a good validity value which is expressed by the accuracy value on sago, river, and domestic wastewater, respectively of 99.86%,

101.38% and 10.59%, while in UV-Vis spectrophotometry, respectively 96.7%, 97.11%, and 98.10%. The precision values obtained are also good in titrimetry for sago samples of $0.31 < 3.02$, domestic samples of $0.15 < 3.50$, and river samples of $2.20 < 4.34$. In the UV-vis spectrophotometric method for sago liquid waste samples of $0.61 < 3.07$, domestic waste of $0.55 < 3.92$ and river samples of $0.013 < 4.54$.

REFERENCES

- [1] Risdianto, D. (2007). Optimization of the coagulation-flocculation process for herbal medicine industry wastewater (a case study of PT. Sido Muncul). Master of Chemical Engineering, Diponegoro University, Semarang.
- [2] Guoqing Wu, W. B. 2011. Determination of Chemical Oxygen Demand in Water Using Near-infrared Transmission and UV Absorbance Method. Chinese Optics Letters, 09(s1).
- [3] Riyanto, P.D. (2014). Test Method Validation & Verification Compliant with ISO/IEC 17025 Testing and Calibration Laboratory. Deepublish
- [4] Harmita. 2004. Review of Article Guidelines for Implementing Method Validation and Calculation Methods. Journal of Pharmaceutical Science Magazine, 1(3), 117-135.
- [5] Hasanah, U., Mulyati, A. H., 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.
- [6] Ramadhan, I., Rohyami, Y., & Ahdiaty, R. (2022). Verification of COD Test Method by UV-Vis Spectrophotometry for Low Concentration and High Concentration. Indonesian Journal of Chemical Analysis (IJCA), 5(1), 52-61.
- [7] Mulyati, A.H., Heliawati, L., Sutanto, Hasanah, U., (2020). Development of Cod (Chemical Oxygen Demand) Analysis Method in Wastewater Using Spectrodirect, Journal of Science Innovare, 3(2).

- [8] Zhang, S., Chen, W., Liu, Y., Luo, P., & Gu, H. (2018). A Modified Method for the Accurate Determination of Chemical Oxygen Demand (COD) in High Chloride Oilfield Wastewater. *Open Journal of Yangtze Oil and Gas*, 3(04), 263.
- [9] Gnanavelu, A., Shanmuganathan, T. S., Deepesh, V., & Suresh, S. (2021). Validation of a Modified Procedure for the determination of Chemical Oxygen Demand using the standard dichromate method in industrial wastewater samples with high calcium chloride content. *Indian J. Sci. Technol*, 14(29), 2391- 2399.
- [10] 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.
- [11] Kurniawati, P., & Alfannah, H. (2019). Comparison of Methods for Determining Permanganate Levels in Faucet Water by Titrimetry and UV Spectrophotometry. *IJCA (Indonesian Journal of Chemical Analysis)*, 2(2), 60-65.
- [12] Sutanto and Kierina, 2019; Cosmetic Liquid Waste Treatment by Electrocoagulation Batch System, *Ecology*, 19(2): 44-54