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Performance test for COD determination in wastewater using a closed reflux method with a COD reactor

DITA SETIAWATI[1], YURIS DIKSY[2,*], ARDINA PURNAMA TIRTA[2]

[1]Prodi Pengolahan Limbah Industri, Politeknik AKA Bogor, Bogor, Indonesia
[2]Prodi Analisis Kimia, Politeknik AKA Bogor, Bogor, Indonesia

*Corresponding author: *yurisdiksy@gmail.com*

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ABSTRACT

Chemical Oxygen Demand (COD) is one of the test parameters to determine the water quality index. In environmental monitoring, valid test results of wastewater parameters are very important as a basis for making environmental policies. In this study, the determination of COD in wastewater refers to SNI 6989.73:2019 Determination of COD by Closed Reflux Titrimetric Method. The performance test of the COD determination method in wastewater samples was conducted on the parameters of precision, accuracy, and uncertainty estimation calculation of the bottom-up method, which was then compared to the acceptance criteria set by the laboratory. The performance test results for COD determination using the closed reflux method by titrimetry yielded a precision value with a percentage RSD of 3.33%; the accuracy test using the spiking technique was within the recovery range of 87-94%, and a relative uncertainty value of 7.23% at a COD concentration of 43.16 mg/L. All performance parameters of the method met the established acceptance criteria. COD determination using the closed reflux method in wastewater can be used for routine analysis.

Keywords: *Accuracy, Chemical Oxygen Demand, method performance, precision, titrimetric, uncertainty estimation*

INTRODUCTION

Wastewater is water that has already experienced a decline in quality due to human actions, which will have adverse effects if not managed properly (Gufran & Mawardi, 2019). Industrial wastewater comes from a series of industrial process activities in the form of liquid, solid, and gas. Wastewater practices contribute to nutrient loading in coastal areas, which could severely impact marine ecosystem health and local communities (Maggs et al., 2024). This wastewater must be treated first so that it does not pollute aquatic ecosystems. Meanwhile, wastewater originating from household activities is generated from household activities such as cooking, washing, and other routine activities (Askari, 2015). Household wastewater is a major source of pollution in urban areas (Budi, 2000).

Wastewater components contain substances or materials that can endanger human life and disrupt the environmental ecosystem (Hassan, 2024; Harsanto et al., 2024). The sources of wastewater pollutants can be organic and inorganic compounds (Poblete et al., 2020). Organic and inorganic substances dissolved in wastewater can reduce water quality if their concentration exceeds the required quality standards. Chemical Oxygen Demand (COD), a pollutant used as an indicator of wastewater quality, and Biological Oxygen Demand (BOD) are two significant indicators of wastewater pollution (Elham et al., 2024; Rachmawati et al., 2024). Biological Oxygen Demand (BOD) is the oxygen required biologically. Chemical Oxygen Demand (COD) is defined as the equivalent amount of oxygen required to oxidize the organic materials present in the water (Cristea et al., 2014).

The oxidation of organic materials in water through chemical processes requires oxygen in the decomposition process, which leads to a decrease in the oxygen present in the water (Pamungkas, 2016). The increase in COD indicates an increase in organic matter in domestic wastewater (Listianti & Sutanto, 2024; Prianggono et al., 2024). The concentration of COD in water is greatly influenced by the sources of waste produced. Physically, a high COD value can be seen from the color and odor of wastewater. The higher the concentration of color produced and the unpleasant smell, the higher the COD value of the wastewater (Satmoko, 2014). Wastewater with a high COD value should not be discharged into aquatic ecosystems before being treated first because it will pollute the aquatic ecosystem. This is in accordance with government regulations based on Government Regulation No. 22 of 2021 concerning the Implementation of Environmental Protection and Management. Therefore, the analysis of COD levels in wastewater needs to be conducted.

Analysis of COD can be determined using several methods, namely the open reflux method (Jannah, 2021), closed reflux using UV-Vis spectrophotometry (Ramadhan, 2022), electrochemistry (Diksy et al., 2020), and sensors (Zhimin et al., 2022). The electrochemical determination of COD has been widely developed and is considered safer because it does not use hazardous

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chemicals. However, this electrochemical method has not yet been mass-produced. Testing laboratories generally use spectrophotometry and titrimetry methods. Both methods have their advantages and disadvantages. The determination of COD using a spectrophotometer has better sensitivity and requires less chemical usage, but in turbid samples, it can cause significant matrix interference. In the titrimetric method, sophisticated instrumentation is not required, and it is more accurate for various types of samples (Dedkov et al., 2000; Gnanavelu et al., 2021). Both titrimetric and spectrophotometric methods require sample preparation beforehand, which involves oxidation processes with open or closed reflux. The closed reflux method is preferred because it has a stable reaction, is safer, and has higher accuracy (Potter & Waller, 2004).

In environmental monitoring, valid test results of wastewater parameters are crucial as a basis for formulating environmental policies. Therefore, the analysis methods in testing wastewater parameters need to be performance-tested to provide evidence that the laboratory can produce valid and accountable data (Tirta et al., 2023). In this study, the performance of the COD determination method using the closed reflux method was tested titrimetrically. This method refers to SNI 6989.73:2019 Determination of COD by Closed Reflux Titrimetric Method. The performance test of the method is conducted on the parameters of precision, accuracy, and uncertainty estimation calculation. The results of the method's performance test will be compared against the standards used by the laboratory.

METHODS

Material and Equipment

The research materials used consist of test materials and chemicals. The test material used is wastewater from the laboratory in AKA Bogor. The chemicals used are ferro ammonium disulfate hexahydrate (Merck), potassium hydrogen phthalate (Merck), Potassium dichromate (Merck), ferroin indicator, 0.1 N potassium dichromate standard solution (digestion solution), sulfuric acid reagent solution (a mixture of Ag_2SO_4 and H_2SO_4), and aquabidest.

The tools used in this research include main tools and supporting tools. The main equipment used includes the COD Reactor (HACH DRB 200) and a 10 mL microburette with a minimum scale precision of 0.02 mL. The supporting equipment used includes a 10 mL tube, a 5 mL volumetric pipette, a 10 mL Mohr pipette, and a 250 mL beaker.

Methodology

The methodology consists of reagent preparation, method performance testing, and statistical data processing. The performance test of the COD determination method in wastewater samples was conducted on the parameters of precision, accuracy, and uncertainty estimation calculation of the Bottom-up method.

Preparation of 0.1 N Digestion Solution

$K_2Cr_2O_7$ that has been dried in an oven for 2 hours at 150°C was weighed at 4.903 g and then dissolved in 500 mL of organic-free water, 167 mL of H_2SO_4(p), and 33.3 g of $HgSO_4$, then made up to 1000 mL with aquabidest.

Standardization of 0.05 N FAS Solution

The volume of 5 mL of 0.05 N potassium dichromate solution is pipetted into an Erlenmeyer flask, then 2 mL of concentrated H_2SO_4 and 1-2 drops of ferroin indicator are added. The solution is then titrated with 0.05 N FAS solution until the endpoint of the titration is marked by a red-brown color.

Determination of COD Content

The volume of 1.5 mL of digestion solution, 2.5 mL of sulfate solution, and 2.5 mL of sample solution are placed into an ampoule tube and homogenized. The solution is refluxed at 150° C for 2 hours, then cooled and transferred to a 250 mL Erlenmeyer flask. 1-2 drops of Ferroin indicator are added, and then titrated with 0.05 N FAS solution until the endpoint is reached, indicated by a color change from blue-green to red-brown color.

Method Performance Test

Precision (Repeatability) Test

Seven sample solutions were prepared according to the sample testing procedure. Then the percentage RSD (Relative Standard Deviation) or %RSD value is calculated using equation (1)

$$\%RSD = \frac{SD}{x} \text{ X } 100\% \quad (1)$$

where SD is the standard deviation and x is the average result of the COD concentration determination.

Accuracy Test

The accuracy test is conducted similarly to the sample precision determination, but before that, a spiking technique is performed by adding a standard KHP solution (100 mg O_2/mL) to the sample and then titrating with a 0.05 N FAS solution. The percentage recovery (%Recovery) is calculated using equation (2)

$$(\% \text{ recovery}) = \frac{C3\text{-}C1}{C2} \text{ X } 100\% \quad (2)$$

where C1 is the concentration of the unspiked sample, C2 is the concentration of the added COD standard, and C3 is the COD concentration in the mixture of the sample and the standard spike.

Uncertainty Estimation

The estimation of uncertainty in COD determination using closed reflux titrimetry is conducted using the bottom-up method. The sources of uncertainty contributing to the errors in COD determination are identified from the processes of standard solution preparation, sample pipetting, oxidation in closed reflux, and sample titration.

RESULT AND DISCUSSION

Chemical Oxygen Demand (COD) is used to determine the amount of oxygen required to oxidize organic matter in wastewater samples. Table 1 shows the performance test results of the COD determination method with closed reflux titrimetry, with precision, accuracy, and uncertainty estimation parameters meeting the requirements.

Table 1. Data results of performance testing of COD determination method with closed reflux by titrimetry.

Test Parameter	Value	Acceptance criteria	Reference standard	Result
Precision (43.16 mg O_2/L)	0.9978	%RSV<0.5 CV Horwitz	SNI 6989 73:2009	according to acceptance standards
Accuracy	%Recovery = (89-94)%	%Recovery = (86-94)%	SNI 6989 73:2009	according to acceptance standards
Uncertainty estimation (43.18 ± 3.12) mg O2/L	Relative uncertainty = 7.22%	Relative uncertainty < % CV Horwitz (13.48%)	Internal Laboratory	according to acceptance standards

Precision

Precision is the closeness between test results conducted independently in the shortest possible time under relatively the same conditions. (Cantwell, 2025). The precision test conducted is a repeatability test performed by a single analyst seven times in the same laboratory using the same equipment and conducted on the same day. The results of the precision test are expressed in the value of relative standard deviation percentage (%RSD). The results of the precision tests can be seen in Table 2.

Table 2 shows the results of the precision test of the COD analysis method in wastewater with closed reflux by titration, yielding a %RSD value of 3.33%. The results of this precision test have met the acceptance criteria based on SNI 6989.73: 2009, which is %RSD ≤ 5%. The precision value indicates the random errors occurring in the method. Random errors, also known as indeterminate errors, are errors whose values cannot be predicted, have no governing rules, and fluctuate (Cantwell, 2025). The precision value indicates the extent to which the measurement results have been determined without reference to the true value. Precision accuracy leans more towards the understanding of result consistency. The random errors that occur must fall within the acceptable value range required by SNI 6989.73: 2009. In the determination of COD with closed reflux titrimetry, sources of random error can arise from the instability of electrical current voltage in the COD reactor, the purity level of chemicals, contamination variations, and environmental variations. (fluctuations in temperature or humidity). Random errors cannot be eliminated, but they can be minimized by increasing the number of tests.

Table 2. Results of precision test for COD determination method with closed reflux by titrimetry.

Repetition	Blank Titration Volume (mL)	Sample Titration Volume (mL)	M FAS	Sample Volume (mL)	Concentration COD (mgO_2/L)
1	3,400	3,083	0.043	2.50	43.52
2	3,400	3,100	0.043	2.50	41.18
3	3,400	3,083	0.043	2.50	43.52
4	3,400	3,100	0.043	2.50	41.18
5	3,400	3,083	0.043	2.50	43.52
6	3,400	3,075	0.043	2.50	44.62
7	3,400	3,075	0.043	2.50	44.62
Average					43.61
Standard deviation					1.4395
%SBR					33.33

Accuracy

Accuracy is the value that indicates how close the measurement results are to the actual value. The accuracy value reflects a value that is proportional to the precision of the actual results (Cantwell, 2025). Accuracy testing can be conducted in several ways, including the measurement of Certified Reference Material (CRM), Standard Reference Material (SRM), comparison of different sample quantities, spiking method, and comparative testing. In this experiment, accuracy testing was performed using the spiking technique, which involved adding a standard KHP solution to the sample with seven repetitions. The accuracy value is expressed as the percentage recovery (%Recovery) against the added standard concentration. The results of the accuracy test for COD determination using closed reflux titrimetry can be seen in Table 3.

Table 3 shows the % recovery values obtained from the determination of COD with closed reflux titrimetrically in the range of 87-94%. The results of this accuracy test have met the acceptance criteria based on SNI 6989.73: 2009, which is that the %recovery falls within the range of 85-115%. The % recovery values indicate systematic error. Systematic errors are constant errors. Systematic errors can be caused by several factors, including uncalibrated equipment, the failure to use correction values from instrument calibration, evaporation, diffusion, absorption, or adsorption of the analyte in the test sample being analyzed, non-selective methods, and interference from the sample matrix (Cantwell, 2025).

Table 3. Results of acccuracy test for COD determination method with closed reflux by titrimetry.

Repetition	Sample COD concentration (mg/L O_2)	Standard COD concentration (mg/L O_2)	Concentration of COD sample + spike (mg/L O_2)	%Recovery
1	43.16	137.28	171.60	93.56
2	43.16	137.28	163.02	90.24
3	43.16	137.28	171.60	93.56
4	43.16	137.28	163.02	90.24
5	43.16	137.28	171.60	93.56
6	43.16	137.28	163.02	87.31
7	43.16	137.28	163.02	87.31

Uncertainty Estimation

Estimation of measurement uncertainty is a parameter that establishes a range of values within which the true measured value is estimated to lie. The value of this uncertainty combines the true value and all possible errors that may occur in chemical measurements, both random and systematic errors, into a single value. In chemical testing and measurement, we cannot ensure whether the obtained value is the true measurement value because there is a possibility of contributing error factors in the measurement. Thus, an uncertainty estimation measurement was conducted so that the test results fall within a certain range where the true value lies. In ISO 17025:2017 clause 7.6, it is also mentioned that laboratories must identify contributions to measurement uncertainty.

In addition, the estimated measurement uncertainty value must be evaluated against certain acceptance criteria, such as the CV Horwitz. When evaluating measurement uncertainty, all significant contributions, including those arising from sampling, must be accounted for using appropriate analytical methods. Estimation of uncertainty in COD determination with closed reflux titrimetry is performed using the bottom-up method. The sources of uncertainty contributing to the error in COD determination are identified from the sample pipetting process, oxidation under closed reflux conditions, and the sample titration process. The sources of uncertainty contributing to the error are illustrated in Figure 1.

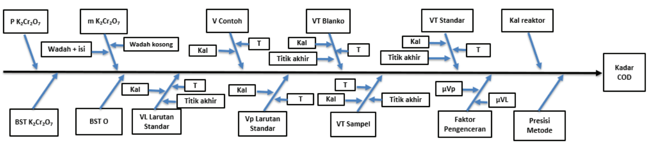

Figure 1. Fishbone Diagram of Uncertainty Estimation COD determination with closed r reflux titrimetry.

The standard uncertainty sources contributing to the error are calculated individually, then combined into the combined uncertainty. The expanded value of the combined uncertainty is calculated to account for unquantified uncertainty sources. The results of the uncertainty estimation calculations for COD determination using the closed reflux method by titrimetry can be seen in Table 4.

Table 4. Results of COD analysis uncertainty estimation.

Symbol	Value (x)	Standard uncertainty (µx)	Combined standard uncertainty (µ/x)2
P $K_2Cr_2O_7$	1	0.00033	1.111E-07
m $K_2Cr_2O_7$	245.9	0.00049	4.0518E-12
BST $K_2Cr_2O_7$	49	0.00023	2.2714E-11
BST O	8	000009	1.1719E-10
VL std	100	0.08372	7.0083E-07
Vp std	5	0.00918	3.3675E-06
VT blk	3.4	0.02264	4.4341E-05
VT std	5.825	0.02282	1.5349E-05
VT spl	3.085571	0.02262	5.3760E-05
Vp spl	2.5	0.01739	4.8368E-05
FP	5	0.01818	1.3215E-05
Cal Reactor	150	0.50000	1.1111E-05
Precision	43.16	1.44011	1.1121E-03
Total Combined Uncertainty			1.56
Expanded Joint Uncertainty			**3.12**

Table 4 shows the extended combined uncertainty value of 3.12 mg O_2/L for a COD concentration of 43.18 mg O_2/L in the tested sample. This combined uncertainty value is the absolute uncertainty value for the COD concentration in the tested sample. Relative uncertainty is calculated to determine the percentage of uncertainty against the obtained concentration. The results of the uncertainty estimation evaluation can be seen in the following Table 5.

Table 5. Results of Measurement Uncertainty Estimation Evaluation.

COD Sample (mg O_2/L)	Uncertainty (mg O_2/L)	Relative Uncertainty	CV Horwitz (%)
43.16	3.12	7.23	13.48

Table 5 shows the relative uncertainty value of COD analysis by titration at 7.22%. This value meets the laboratory's requirement, which is a relative uncertainty % < CV Horwitz (13.48%). The estimation of uncertainty for COD analysis by titration was performed using the bottom-up technique, with the uncertainty components estimated to originate from 13 components. The distribution of errors from each source of uncertainty can be seen in Figure 2. If plotted in a diagram, the component contributing the largest uncertainty value comes from the method's precision, which is 0.0011.

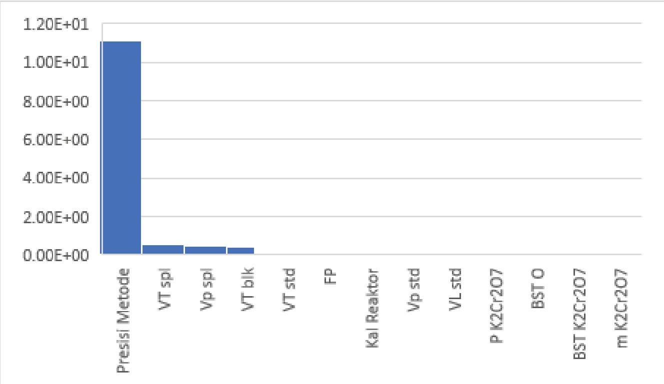

Figure 2. Diagram of COD Analysis Error Distribution in Wastewater Using Closed Reflux Titrimetric Method.

CONCLUSION

The performance test results for COD determination using the closed reflux method with the COD reactor in wastewater provide test results for precision, accuracy, and estimation of testing uncertainty that meet the predetermined acceptance criteria.

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