

# METHOD VERIFICATION OF CHEMICAL OXYGEN DEMAND (COD) AND TOTAL SUSPENDED SOLID (TSS) ANALYSIS FROM MENTAYA RIVER

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**Abstract.** Research has been conducted which were intended to study the feasibility of the method and the quality of Mentaya River water based on chemical oxygen demand (COD) and total solid suspended (TSS) parameters. The method used in this research was based on SNI 6989.73-2009 with the titrimetric for COD analysis and SNI 06-6989.3-2004 using the gravimetric for TSS analysis. The results of verification analysis for precision tests determine COD and TSS by 3.3% and 1.2%, respectively. Approval values for determining COD and TSS were 102% and 97.4%, respectively. Estimated values for COD and TSS from certified reference material (CRM) were  $49.33 \pm 0.1356$  mg/L and  $73.6 \pm 0.3916$  mg/L respectively. The COD results of the Mentaya River at Samuda, Ketapang and Kuayan sections were 34 mg/L, 123.2 mg/L and 8 mg/L respectively. Meanwhile, the TSS results at Samuda, Ketapang, and Kuayan locations were 98 mg/L, 10 mg/L and 32 mg/L respectively. The results of the verification method can be concluded that the method for determining COD and TSS meets the requirements so it can be used regularly in the laboratory. From the COD analysis, the quality of the Mentaya River at the Kuayan section below the quality standard of Indonesian Government Rules No 82 of 2001, while the Samuda and Ketapang sections exceeded the quality standard. The analysis result for TSS of the Mentaya river at Kuayan and Ketapang sections was below the quality standard and the Samuda section exceeded the quality standard of Indonesian Government Rules No 82 of 2001.

## INTRODUCTION

River water quality is strongly influenced by two factors, namely natural factors and human factors. Natural factors that affect the condition of the river such as heavy rain that can overflow and become cloudy, while factors derived from humans such as waste disposal originating from industry, agriculture and cosmetics [1]. These various factors can reduce river water quality, so it is necessary to analyze with various water testing parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), total suspended solids (TSS), fat oil, heavy metals, and others. For this reason, the analysis was delivered for monitoring the Mentaya River in the East Kotawaringin with test parameters, namely COD based on SNI 6989.73-2009 using the titrimetric method [2] and TSS based on SNI 06-6989.3-2004 by the gravimetric method [3].

Chemical Oxygen Demand (COD) is the amount of oxygen needed to decompose all organic matter contained in water which is intentionally decomposed chemically by using potassium bicarbonate as strong oxidizer under acidic and hot conditions with a silver sulfate catalyst, so all kinds of organic materials which are easily decomposed or complex and difficult to decompose will be oxidized [4]. In addition to carrying out the COD test to find out the water level, a TSS test can also be carried out. The TSS in the water is in the form of organic and inorganic materials which can be filtered with 0.45  $\mu$ m porous millipore paper [1].

River water with high COD and TSS values cannot be used as drinking water or household needs. It is necessary to analyze the level of both parameters to determine the quality of the Mentaya River. However, before the method is needed to be verified before being carried out. Verification of this method is carried out by following the quality management system of the Indonesian National Standard which requires testing laboratories to analyze materials using valid measurement methods to obtain valid testing data [5]. Method verification is an act of research on certain parameters based on laboratory experiments, to prove that the method meets the requirements for its use [6]. The parameters tested in the verification method for determining the COD and TSS levels were precision, accuracy, and uncertainty measurement. Precision was done to determine the closeness or compatibility between the test results with one another in a series of tests [7], meanwhile, accuracy was a measure that showed the degree of closeness of the results of analysts with the actual levels of the analyte [8]. Verification of this method is carried out using materials traced to international units using Certificate Reference Materials (CRM).

## MATERIALS AND METHOD

### Materials

The reagent used all were analytical grade such as CRM catalog 516 solutions made by ERA, CRM solution 4032 made by ERA, ferrous ammonium sulfate (Merck),  $K_2Cr_2O_7$  (Merck),  $HgSO_4$  (Merck), concentrated  $H_2SO_4$  (Merck),  $Ag_2SO_4$  (Merck), ferroin indicator, Whatman filter paper, and distilled water.

### Instrumentations

The equipment used was an analytical balance (Ohaus), oven (Shel Lab), burette (Pyrex), desiccator (Iwaki), test tube (Iwaki), vacuum Pipe (Vacuubrand) and Glassware (Pyrex).

### Methods

#### *Method for Determining Chemical Oxygen Demand (COD)*

The test sample is preserved by adding concentrated  $H_2SO_4$  until the pH is smaller than 2 and the sample is stored in a cooler at 4 °C with a recommended maximum save the time of 7 days.

#### *Standardization of Ferro Ammonium Sulfate Solution*

Five milliliters of  $K_2Cr_2O_7$  0.1N was put into Erlenmeyer flask and added 2.5 mL of distilled water, then cooled to room temperature. The solution was added 2-3 drops of ferroin indicator and titrated with ferric ammonium sulfate (FAS) solution.

#### *Determination of COD (Chemical Oxygen Demand) levels*

Determination of COD level under SNI 6989.73: 2009. A total of 2.5 mL sample was put into a test tube, then 1.5 mL of potassium dichromate and 3.5 mL of sulfuric acid reagent solution. Then close the tube and shake it gently until the sample is homogeneous. The reaction tube was heated at 150 °C for 2 hours then titrated with a 0.05 M FAS solution with the addition of 3 drops of ferroin indicator until there is a clear color change from green to reddish-brown. The COD value can be calculated by the following formula:

$$COD = \frac{(A-B) \times M \times 8000}{V}$$

A = Volume of FAS solution needed for blank (mL)

B = Volume of FAS solution needed for the test sample (mL)

M = Molarity of FAS solution

V = Sample volume (mL)

### Determination of TSS (Total Suspended Solid) levels

Filter paper is placed on filtration equipment. Install the vacuum and washing container with 20 mL of excess distilled water. Continue suctioning to remove all remaining water, turn off the vacuum and stop the spraying. Then the filter paper that has been rinsed with distilled water is put into a porcelain dish and inserted into the oven at 105 °C for 1 hour. After the heating process, the filter paper is cooled into the desiccator for 20 minutes, then weighed until a constant is obtained. Meanwhile, for CRM preparation, the CRM solids are inserted into a sterilized 1000 mL volumetric flask then added distilled water to 1000 mL and shake until homogeneous, then put in bottles that have been sterilized and stored in an incubator.

The test sample is preserved at 4 °C and should be stored no more than 24 hours. The determination of TSS levels is following SNI 06-6989.3-2004. Filtering is done with vacuum equipment, then filter paper which is known to be heavy is placed on filtration equipment and filter paper is rinsed with distilled water. The test sample is stirred with a magnetic stirrer to obtain a homogeneous test sample. The test sample is taken 50 mL which is poured on filter paper then the pipette used is rinsed with distilled water. The filter paper is taken and heated into the oven at 150 °C for 1 hour. After the heating process, the filter paper is cooled into the desiccator for 20 minutes, put filter paper into analytical balance until a constant weight is obtained. This TSS value can be calculated by the following formula:

$$TSS = \frac{(A-B) \times 1000}{V}$$

A = weight of filter paper + dry residue (mg)

B = weight of filter paper (mg)

V = Sample volume (mL)

### Precision and Accuracy Test

Precision was determined by repeating COD and TSS testing using CRM 5 times, meanwhile for accuracy test by comparing the values obtained from testing COD and TSS with the actual values in the CRM certificate.

## RESULTS AND DISCUSSION

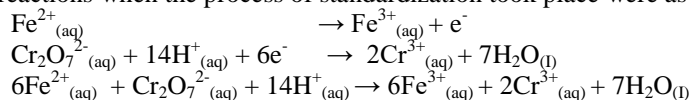
Chemical Oxygen Demand (COD) and Total Suspended Solid (TSS) are routine analysis that is often carried out to monitor the quality of Mentaya River at East Kotawaringin. The verification of this method aims to prove that the method has met the requirements for its use. In addition to verifying the method, this test also tested the water quality of the Mentaya River due to its usage in many aspects. The verification method is carried out using certified materials that belong to international units produced by ERA with catalog number 516 for COD CRM and catalog number 4032 for TSS CRM materials. The parameters used for the verification method are precision, accuracy, and uncertainty estimation.

The COD analysis is using the volumetric method by SNI 6989.73-2009. In COD test, ferrous ammonium sulfate is used as a titrant, so that the solution must be standardized firstly. Standardization of solutions is a process when the concentration of a secondary standard solution is precisely determined by titrating with a primary standard solution [9]. Standardization functioned to determine the exact concentration of a secondary standard solution. A standard solution is a solution whose concentration is known with certainty and accuracy. There are two types of standard solutions, namely primary and secondary standard solutions. The primary standard solution is a substance that has known purity, the concentration could be known with certainty and meticulous based on dissolved substances. The secondary standard solution is an impure substance or its purity is unknown, the concentration of the solution was possibly known through the standardization process.

**TABLE 1.** Standardization of ferrous ammonium sulfate

Volume of K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> 0,1 N (mL)	Titration volume (mL)	Average volume (mL)
5	10.6	
5	10.5	10.57
5	10.6	

Based on Table 1, the average volume for titrating 0.05 M ferrous ammonium sulfate solution was 10.57 mL so the exact concentration obtained by standardization was 0.047 M. Standardization is an important step to determine the right concentration of ferrous ammonium sulfate solution. Ferro ammonium sulfate is standardized with potassium dichromate which is the standard primary solution. The indicator used in this standardization process is the ferroin indicator. The reactions when the process of standardization took place were as follows:



Those reactions were based on the reduction-oxidation process between  $\text{Fe}^{2+}$  and  $\text{Cr}^{6+}$  ions, with the assistance of indicator the reaction will finish after the color change of solution.

For the COD analysis of Mentaya River was carried out at 3 sampling locations, namely Samuda Village, Ketapang District, and Kuayan Village. The results can be seen in Table 2.

**TABLE 2** Results of COD Levels from Mentaya River

Sampling location	Class II Water Quality Standards (Government Regulation No.82, 2001)	COD level (mg/L)
Samuda	25 mg/L	34
Ketapang	25 mg/L	123.2
Kuayan	25 mg/L	8

Based on Table 2, Ketapang District had the highest COD level from other location, since that district had a lot of community activities, such as a rubber factory and the presence of electric steam power plant. The community activities affected the quality where people used river water as a place for bathing, washing and defecating. The rubber factory produced liquid waste in the form of organic compounds, which in the process of decomposition required oxygen. The existence of an electric steam power plant contributed pollutants in the form of temperature change (for example heat) that came from power plant waste which used river water as a cooler. This kind of pollutant caused the rise of water temperature that was not suitable for aquatic life (organisms, fish, and plants in water). Plants, fish, and dead organisms would break down into organic compounds, so the decomposition process of these organic compounds required oxygen, resulted in a decrease in oxygen content in water [10]. In Samuda Village, river water had relatively high COD levels, where this location was close to the palm oil industry. The industry produced crude palm oil (CPO) waste containing fatty alcohols, methyl esters, saturated and unsaturated fatty acids. The CPO layer inhibited the diffusion process of free oxygen to the surface of the water so the dissolved oxygen content was drastically reduced [11]. Meanwhile in Kuayan Village had the lowest COD level due to Kuayan was far from residential and industrial settlements, meaning minimum people activity and industrial waste that affected river water. Based on Government Regulation No. 82 of 2001, concerning the water quality standard for COD level is 25 mg/L High level of COD were not desirable for fisheries and agriculture because indicated the presence of organic pollutants in large quantities, causing the dissolved oxygen content in water to be low, making oxygen as a source of life for aquatic creatures (animals and growing plants) cannot be fulfilled and bringing death [12].

Besides COD, the analysis of TSS would bring information related to the number of suspended solids in the water. The TSS analysis was described in Table 3.

**TABLE 3** Results of TSS Levels from Mentaya River

Sampling location	Class II Water Quality Standards (Government Regulation No.82, 2001)	TSS level (mg/L)
Samuda	50 mg/L	98
Ketapang	50 mg/L	10
Kuayan	50 mg/L	32

The Samuda Village had the highest TSS level and quite a large result. This could happen since in the Samuda there is an oil palm industry that produced organic waste that could not dissolve in river water. The other factor like soil erosion due to rain, water movement in the form of tidal currents will be able to stir up existing sediment and when sampling river water is receding [1]. High TSS levels were not always from organic matter but also consist of mud and fine sand. The Ketapang and Kuayan locations had lower TSS levels than in Samuda since Kuayan far from residential areas and industries. Although Ketapang area closed to residential areas and industries, it has a low TSS

level. The minimum of TSS levels because organic compounds obtained from industrial and domestic waste were not all insoluble organic substances (suspended solids), but also dissolved organic substances. Therefore it is necessary to conduct total dissolved solids (TDS) in terms of finding out which substances are dissolved because TSS can only know the suspended solids. The high content of TSS in the water affected the power of light penetration where prevents the entry of sunlight into the water, so that will disrupted the process of photosynthesis and caused the drop in dissolved oxygen released into the water by plants. The low dissolved oxygen in river water will cause fish to die [13].

As mentioned before, there are 2 parameters to evaluate the result of method validation namely precision and accuracy. Precision is a measure that shows the degree of conformity between individual test results, measured by the spread of individual results from the average if the procedure is applied repeatedly to samples taken from a homogeneous mixture. Precision tests are conducted to determine the closeness or suitability between the results of the tests with each other in a series of tests. Each method is determined by titrimetric of COD and gravimetric of TSS by doing 5 times in replication. Precision can be expressed as repeatability or reproducibility. Precision values are calculated using the standard deviation (SD) to produce a relative standard deviation (RSD) or coefficient variation (CV). Careful criteria are given if the method gives the % RSD value of  $\leq 2\%$ . The results of the determination of precision can be seen in Table 4.

**TABLE 4** Precision test for COD and TSS Catalog 516 and 4032

Repeatability	COD level (mg/L)	TSS level (mg/L)
1	48.12	74
2	48.12	74
3	48.12	74
4	51.40	72
5	51.40	74
$\sum (x - \bar{x})^2$	12.28	3.20
SD	1.65	0.89
%RSD	3.34	1.21
CV Horwitz	8.37	8.89

Based on Table 4 shows that the standard deviation (SD) value obtained at COD levels was 1.65 mg/L and obtained a relative standard deviation (RSD) value of 3.34%. The RSD value obtained exceeded the maximum requirement of  $\leq 2\%$  so it must be compared with the value of CV Horwitz. The CV Horwitz value obtained was 8.37 so that it can be stated that the test is precisely because of the % RSD value less than CV Horwitz. The result indicated that the method used for determining COD by titrimetric meets the requirement of precision. Meanwhile, the SD value on TSS was much lower from COD, and the result also confirmed that the gravimetric method was suitable for the analysis of TSS as a routine method.

Accuracy is the closeness of the test results between the results obtained with the actual value or the reference value [10]. Accuracy is expressed as the percentage of recovery of the standard added into a sample solution. To achieve high accuracy is possible doing many ways such as using calibrated equipment, good reagents and solvents, temperature control and careful implementation, compliance with procedures according to the procedure [14].

Accuracy describes a systematic error from a measurement result. Systematic errors come from influences that can be known with certainty and are constant. Source of error can be from moisture, reference material, and uncertainty. The results of accuracy from COD and TSS can be seen in Tables 5 and 6.

**TABLE 5** Accuracy test for COD CRM 516

Repeatability	Test value (mg/L)	True value in certificate (mg/L)	% Accuracy
1	48.12	50.9	94.54
2	48.12	50.9	94.54
3	48.12	50.9	94.54
4	51.14	50.9	100.47
5	51.14	50.9	100.47
Average	49.33	50.9	96.91

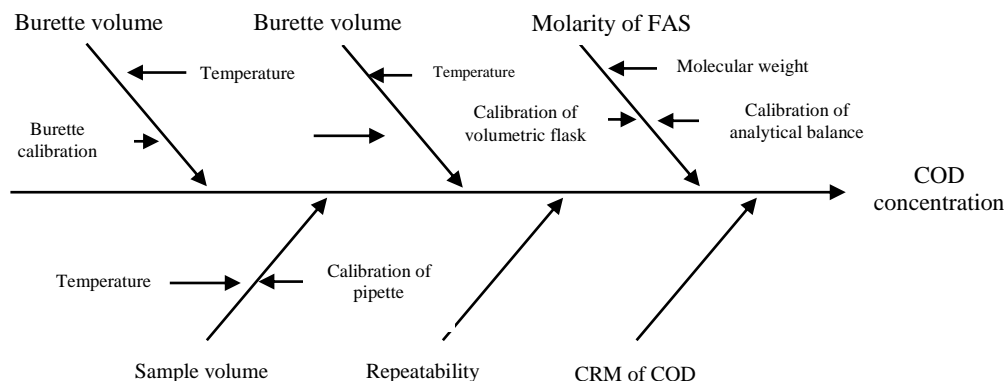
**TABLE 6** Accuracy test for TSS CRM 4032

Repeatability	Test value (mg/L)	True value in certificate (mg/L)	% Accuracy
1	74	75.5	98
2	74	75.5	98
3	74	75.5	98
4	72	75.5	95
5	74	75.5	98
Average	73.6	75.5	97.4

Tables 5 and 6 pointed the accuracy was delivered by comparing the average measurement/testing results with the true value in 5 times replication. The accuracy value was expressed by % trueness since CRM used as a sample test. Based on the Association of Official Analytical Chemist (AOAC), the range of % accuracy that meets the requirement is 80-115%. The average of % accuracy for COD and TSS analysis respectively was 96.91% and 97.4% and both of the results were acceptable with AOAC and the method showed good accuracy.

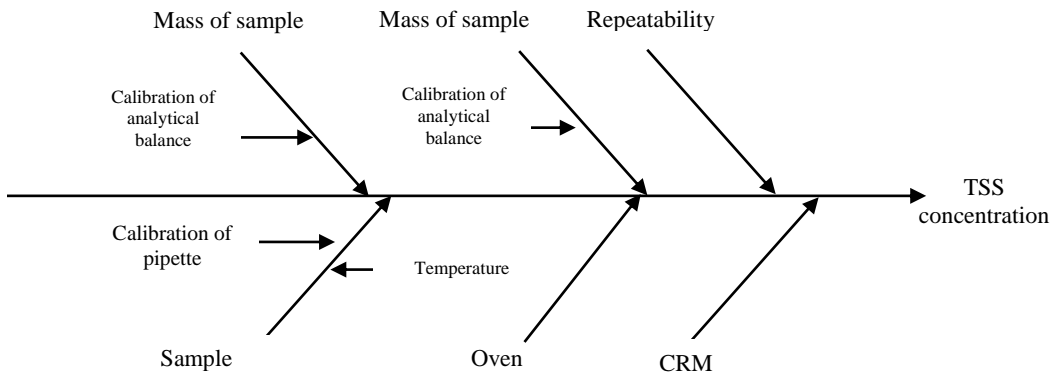
#### *Uncertainty Measurement*

Measurement uncertainty is a range of values obtained from a collection of several deviations. The value of uncertainty is measured to determine and ensure the result of the verification method for COD and TSS can be justified and the method used can provide valid results. Measurement of uncertainty originated from many factors that affected the result, besides that it can determine how much value can be reported with valid data. Determination of uncertainty value was done by analyzing sources that have the potential to provide uncertainty in measurement from the beginning of a material downturn to the reading of tools, and the ability of analysts. The stages of determining uncertainty were by making the fishbone diagram.



**FIGURE 1. Fishbone diagram of COD uncertainty measurement**

The fishbone diagram in Figure 1, six (6) sources possibly affected the estimated uncertainty value of verification method for COD such as burette volume (A), burette volume (B), FAS molarity, sample volume, repeatability referred to precision test, and CRM of COD which belongs to accuracy test. There were two sources of burette volume since the analysis for COD was using different burette.



**FIGURE 2. Fishbone diagram of TSS uncertainty measurement**

Meanwhile, the fishbone diagram in Figure 2 contains 6 sources that might affect the TSS result, namely mass sample (A), mass sample (B), sample volume, calibration of oven, repeatability, and CRM source.

*Standard Uncertainty in Determining COD*

The standard uncertainty in determining the level of COD is based on factors that are considered to contribute to the value of measurement uncertainty which can be seen from Figure 1. The uncertainty value obtained from each source is used to calculate the value of the combined uncertainty as described in Table 7.

**TABLE 7** Standard and Combined Uncertainty of COD test

Uncertainty source	Value (x)	Unit	Standard uncertainty ( $\mu x$ )	Relative standard uncertainty ( $\mu x/x$ )	$(\mu x/x)^2$
Burette 25 mL	3.12	mL	0.00838	0.0026	$7.2160 \times 10^{-6}$
Burette 25 mL	2.79	mL	0.00834	0.0029	$8.9319 \times 10^{-6}$
Volumetric pipette 5 mL	2.5	mL	0.01508	0.0060	$3.6367 \times 10^{-5}$
Molarity of FAS	0.047	mol/L	0.00067	0.0141	0.0002
CRM COD	50.9	mg/L	0.217	0.0042	$1.8175 \times 10^{-5}$
Repeatability	1		0.0334	0.0334	0.0011

The result of the estimated combined uncertainty was 0.0684 mg/L and can be obtained as the following equation:

$$\frac{\mu \text{COD}}{\text{level}} = \sqrt{\frac{(\mu \text{burette})^2}{\text{burette}} + \frac{(\mu \text{burette})^2}{\text{burette}} + \frac{(\mu \text{volumetric pipette})^2}{\text{pipette volume}} + \frac{(\mu \text{molarity})^2}{\text{molarity}} + \frac{(\mu \text{CRM})^2}{\text{CRM}} + \frac{(\mu \text{repeatability})^2}{\text{repeatability}}}$$

The estimated value of expanded uncertainty can be obtained from the combined uncertainty value multiplied by the coverage factor (K), which is two, and resulted in 0.1356 mg/L. Coverage factor (K) was chosen from the 95% confidence level to get expanded uncertainty. Based on the result, the calculation of uncertainty in determining the COD level was  $49.33 \pm 0.1356 \text{ mg / L}$ . The obtained value was still below the level set by the sample which indicated that the uncertainty value still gave good results.

*Raw Uncertainty in Determining TSS*

The raw uncertainty in determining the level of TSS was based on factors that are considered to contribute to the uncertainty value that can be seen in Figure 2. A similar step likely in COD analysis, all sources have to be combined to figure out the combined uncertainty as described in Table 8.

**TABLE 8** Standard and Combined Uncertainty of TSS test

Uncertainty source	Value (x)	Unit	Standard uncertainty ( $\mu x$ )	Relative standard uncertainty ( $\mu x/x$ )	$(\mu x/x)^2$
Mass (A)	0.108	g	0.00039	0.0036	$1.301 \times 10^{-5}$
Mass (B)	0.104	g	0.00035	0.0034	$1.1531 \times 10^{-5}$
Volumetric pipette 25 mL	25	mL	0.0422	0.0016	$2.8504 \times 10^{-6}$
Oven	150	$^{\circ}\text{C}$	1.0632	0.0070	$5.0248 \times 10^{-5}$
CRM TSS	75.5	mg/L	3.725	0.0493	0.00243
Repeatability	1		0.0121	0.0121	0.00014

The result of the estimated combined uncertainty was 0.1956 mg/L and can be obtained as follows:

$$\frac{\mu_{\text{TSS}}}{\text{level}} = \sqrt{\frac{(\mu_{\text{analytical balance}})^2}{\text{analytical balance}} + \frac{(\mu_{\text{analytical balance}})^2}{\text{analytical balance}} + \frac{(\mu_{\text{volumetric pipette}})^2}{\text{volume}} + \frac{(\mu_{\text{Oven}})^2}{\text{Oven}} + \frac{(\mu_{\text{CRM}})^2}{\text{CRM}} + \frac{(\mu_{\text{repeatability}})^2}{\text{repeatability}}}$$

The estimated value of expanded uncertainty is determined by using the combined uncertainty value multiplied by the coverage factor (K), which is two, and resulted in 0.3916 mg/L. Based on the results obtained it can be reported that the result in determining the TSS level was  $73.6 \pm 0.3916$  mg/L. The uncertainty value indicated good results due to still under the value set by the sample level.

It is also possible to figure out the contribution of each source to the uncertainty value for COD and TSS analysis. The contribution result to uncertainty in method verification of COD and TSS can be seen in Table 9 and 10.

**TABLE 9** The contribution percentage to COD uncertainty

Uncertainty source	Contribution (%)
Burette volume (A)	0.52
Burette volume (B)	0.64
Sample volume	1.77
Molarity	14.60
CRM of COD	1.32
Repeatability	81.13

**TABLE 10** The contribution percentage to TSS uncertainty

Uncertainty source	Contribution (%)
Mass sample (A)	0.48
Mass sample (B)	0.52
Sample volume	0.10
Calibration of oven	1.88
CRM of TSS	91.48
Repeatability	5.50

As can be seen from Table 9 and 10, there were different sources which contributed the maximum from each analysis. For the COD analysis, repeatability was the main source in delivering error factor for 81.13%. This source came from the person doing the analysis such as sample preparation and titration. On the contrary, the CRM of TSS became the primary source in delivering the fault to the result. This is due to the uncertainty value in the certificate already gave the high value.

## CONCLUSION

Precision, accuracy, and uncertainty value in the titrimetric for COD and gravimetric for TSS analysis gave good results so it is recommended for routine methods. Meanwhile, the COD and TSS levels at Samuda, Ketapang, and Kuayan were varied greatly because of the different conditions of each location.



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