IJFAC

Indonesian Journal of
Fundamental and Applied Chemistry

Article http://ijfac.unsri.ac.id

Validation Method Rapid Test COD in Water and Waste Water compare with Standard Method as Quality Assurance in Integrated Testing Laboratory-FMIPA of Sriwijaya University

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Abstract

Portable COD test kit used for testing the COD because its low cost, less waste, contaminant free, efficient, simple and traceable to the international unit system. However the method has not yet accepted as a standard method, so it must be validated before applied in the laboratory according to the requirements of ISO / IEC 17025: 2017. In this study, the Rapid Test COD method vario Lovibond (M1) compared with the standard method APHA 5220D.4 (M2). The Rapid Test method modified used APHA reagents (M3) and vice versa (M4) were also studied. Evaluation based on precision values, HorRat whereas accuracy based on recovery value (R). Comparison of test results also conducted against Certified Reference Material values, and Z-score test. The precision test results for each method for both law range and high range gave HorRat values between 0.3-1.3 that meet the precision requirements. Accuracy testing also gave %R meeting the acceptance limit, even though M3 with the lowest %R is 94.17%. For comparison of results with CRM, the M3 method does not meet the acceptance limit, which is UΔ < Δm. But the results of the Z-score Test all methods provide satisfactory accuracy

Keywords: COD test, rapid test, APHA 5220D.4, validation

Abstrak (Indonesian)

Salah satu parameter uji kualitas air adalah COD. Pengujian COD banyak dilakukan meggunakan portable water test kit dengan alasan ekonomis, sedikit limbah, bebas kontaminan, cukup efisien, sederhana dan tertelusur ke sistem satuan internasional. Metode Rapid Test belum diterima sebagai metode baku, sehingga perlu dilakukan validasi metode, sesuai persyaratan ISO/IEC 17025:2017. Pada penelitian ini dilakukan validasi metode pengujian COD meggunakan metode Rapid Test COD vario Lovibond (M1) dibandingkan dengan metode standar APHA 5220D.4 (M2). Modifikasi metode Rapid test menggunakan reagent dari APHA (M3) dan sebaliknya (M4) juga dipelajari. Evaluasi hasil didasarkan nilai presisi yaitu nilai HorRat dan akurasi didasarkan nilai rekoveri (R), perbandingan hasil pengujian terhadap nilai *Certified Reference Material (CRM),* dan uji Z-score. Hasil uji presisi masing-masing metode baik untuk law range dan high range memberikan nilai HorRat antara 0,3-1,3 yang memenuhi persyaratan presisi. Pengujian akurasi juga memberikan nilai rekoveri (%R) memenuhi batas keberterimaan, walupun M3 dengan %R terendah yaitu 94,17%. Perbandingan hasil terhadap *CRM*, metode M3 tidak memenuhi batas keberterimaan yaitu UΔ<Δm. Namun hasil Uji Z-score semua metode memberikan akurasi yang memuaskan.

Kata Kunci: COD test, rapid test, APHA 5220D.4, validasi

Article Info

Received 19 November 2019
Received in revised 28 January 2020
Accepted 30 January 2020
Available online 17 February 2020

INTRODUCTION

COD often used as a measure of pollutants or wastewater in natural resource. Standard method for COD analysis used dichromate ion ($Cr_2O_7^{2-}$) that act as specified oxidant. Dichromate ion ($Cr_2O_7^{2-}$) reduces to the chromic ion (Cr^{3+}) while both organic and inorganic components in sample will be

oxidized, but in most cases the organic component predominates and is of the greater interest[1].

One of procedure for COD analysis is The Standard Methods for the Examination of Water and Wastewater APHA 5220D.4, closed reflux and Colorometric Method. This methods reduce waste problems because the use of metallic salt reagents and generate smaller quantities of hazardous waste, but require homogenization of samples containing suspended solids to obtain reproducible results [1]. This method however, still has disadvantage, it need at least five standards for Calibration Curve and it is generate more quantities of hazardous waste.

Nowadays, to overcome this problem, there are many portable water test kits used for testing the water parameters on situ for both physical, chemical and microbiological parameters. Along with its development, the equipment can be used in laboratories with more economical, fewer waste generated, all reagents in one kit, pre-treatment and preparation more efficient and simple, traceability to international standard and can be compared with the standard methods [2].

Integrated Testing Laboratory - FMIPA University of Sriwijaya uses Rapid Test method for COD analysis, but this is not a standard method, so to ensure that method meets the ISO/IEC 17025-2017 clausal 7.2.1.5 validation must be carried out [3] and the result must compare with standard method of closed reflux and Colorimetric Method[1].

By validating non-standard methods, estimation can be made on the trust level of the test method used. Performance characteristics commonly evaluated during method validation such as selectivity, working range, analytical sensitivity, trueness (bias, recovery), precision (repeatability, intermediate precision and reproducibility) [4]. In this study, trueness or accuracy and precision with repeatability is used as the characteristic of method of validation.

MATERIALS AND METHODS

Materials

Equipments used in this research are: glass beaker, volumetric pipettes, analytical balances, digestion bottles, COD reactors, COD-meters, Lovibond, UV-Vis spectrophotometers, Shimadzu.

The materials used are $K_2Cr_2O_7$, H_2SO_4, $HgSO_4$, Ag_2SO_4, COD Standard solution COD, CRM 8000 mg/L in H_2O, distillation water and COD reagent ready stock reagent Low Range and High Range, Lovibond.

Methods

All procedure follows COD-meter Vario, Lovibond methods[5] and APHA, Standard Methods for the Examination of Water and Wastewater 5220D.4 Closed Reflux, Colorimetric Method[1]. Both of the result were analyzed using statistic equation.

Data Analysis

Data evaluation used equation as follows:

$$\%\text{Trueness} = \frac{\bar{x}}{\mu}100\% \quad \text{.....(1):}$$

$\bar{x}$: Average test result

μ: Value for Certified Reference Material (CRM)

$$RSD_R = \frac{sd}{\bar{x}} \quad \text{.....(2)}$$

$$\text{PRSD}_\text{R} = 2^{1-0.5\,\log C} \quad \text{.....(3)}$$

$$HorRat = \frac{RSD_R}{PRSD_R} \quad \text{.....(4)}$$

RSD_R.....Relative standard deviation of result.

$PRSD_R$....Relative standard deviation of Horwitz equation

$$\Delta m = |C_m - C_{CRM}| \quad \text{.....(5)}$$

Δ_m: Absolute difference between mean measured value and certified value

C_m: Mean measured value

C_{CRM}: Certified value

$$\mu_\Delta = \sqrt{\mu_m^2 + \mu_{CRM}^2} \quad \text{.....(6)}$$

$$U\Delta = \mu_\Delta \text{ x } 2 \quad \text{.....(7)}$$

μ_Δ : Combined uncertainty of result and certified value (= uncertainty of Δm)

μ_m : Uncertainty of the measurement result

μ_{CRM} : Uncertainty of the certified value

UΔ : Expanded uncertainty

$$Z_{score} = \frac{x_i - X}{\sigma_{SDPA}} \quad \text{.....(8)}$$

$$\sigma_{SDPA} = 0{,}02c^{0{,}8495} \quad \text{.....(9)}$$

x_i: *Result average to* $-\ i$

X: *Certified reference material value*, CRM

σ_{SDPA}: Standard deviation for Proficiency Assessment get from Horwitz curve model

c: Weight fraction of result

RESULTS AND DISCUSSION

Linearity

Linearity tests were performed for the APHA (M2) method and the APHA modification method (M4) by using a ready stock reagent. Whereas the Rapid Test COD-meter method (M2) and its modification method using low range and high range reagents from the APHA method (M3) do not use a standard curve. Low range linearity test was done in the range of 0-90 mg/L and high range is in the range of 100-900 mg/L. From the two calculation results obtained for the second method, the analytical response are linear with coefficients of determination (R^2) higher than 0.990 (Table 1).

Table 1. Linear Regression of COD standard

Method	Equation	R^2
M2-LR	Y= 0,00025 + 0,00024	0,992
M2-HR	Y= 0,000305 + 0,000791	0,997
M4-LR	Y=0,0032 + 0	0,996
M4-HR	Y= 0,000382 + 0,045824	0,999

Precision and accuracy

The test for precision and accuracy used Certified Reference Material (CRM) COD with concentration 8000 ± 68 mg/L. Testing were done by measuring 2 different concentrations in the range concentrations, they are 0-90 mg/L for law range and 100-900 mg/L for high range. For the low range the measurement were done using 20 mg/L and 80 mg/L concentrations of COD, while high range using 200 mg/L and 800 mg/L concentrations of COD. Each COD concentration was obtained from dilution of 8000 mg/L of CRM COD solution.

Evaluation of precision value by *Horwitz Ratio*, HorRat which count from equation (4) [6]. The Trueness was count according to recovery (R) and bias of methods and meeting acceptance criteria from tabel of accuracy from AOAC[7]. Trueness can also be determined by comparing the measurement results with the values of certified reference materials (CRM) based on equations (6) and (7) [8]. Result in Table 2 dan 3.

Tabel 2. Accuracy dan precision of COD methods for low range

Metode	C_m	HorRat	% R	**UΔ**	**Δm**
M1	8064,29	0,73	100,80	198,53	64,29
M2	7863,07	1,03	98,29	262,53	136,93
M3	7842,86	1,14	98,04	289,43	271,43
M4	7986,42	1,24	99,83	318,26	178,63

The acceptance criteria of HorRat value under repeatability conditions ranges are between 0.3 and 1.3 [6]. Tables 2 and 3 show all HorRat values of the all methods studied are meet HorRat acceptance criteria which are between 0.3 and 1.3. This shows that the precision of all methods are acceptable.

Tabel 3. Accuracy dan precision of COD methods for low range

Metode	C_m	HorRat	% R	**UΔ**	**Δm**
M1	8027,14	0,53	100,34	152,43	48,78
M2	7978,35	0,62	99,73	171,25	21,65
M3	7533,57	0,64	94,17	169,15	466,43
M4	8100,40	0,69	101,25	189,74	100,40

In Table 2, the percent R in law range concentration is 100.8%, which means the bias method of M1 is 0.8% and the percent R in high range concentration is 100.34%, which means the bias method of M1 is 0.34%. While the bias method of M2, Standard method APHA are -0.27% (LR) and -1.71% (HR). If the result of M1 is compared with M2 shows that the result not significantly different. It can be concluded that both methods are give a good accuration.

The M3 and M4 methods, which are the methods developed, are biased to the respective methods -1.96 (LR); -5.83 (HR); -0.17 (LR) and 1.25 (HR). When considered from the percent error, the M3 method gives the highest error, in law range concentration give -2% of error and high range give 5% of error. However, the bias of the M3 method still meet the acceptance criteria for accuracy, which is between -8% to 5%.

To ensure method performance, the results compared with CRM certified values. This approach takes into account the certified value, the measurement result and their respective uncertainties[9]. These uncertainties are subsequently combined and the expanded uncertainty UΔ is compared to the difference Δm. If $\Delta m \leq U\Delta$ then there is no significant difference between the measurement result and the certified value [8].

Tables 2 and 3 show that the M3 method, the value of $U\Delta \leq \Delta m$ in HR is $169.15 \leq 466.43$. The M3 method is a modification of the Rapid Test COD-meter method. The LR and HR reagent from the APHA standard method replaces the reagent ready stock. This shows that there are a significant difference between the results of testing the M3 method for HR with the value of the CRM certificate, thus the M3 method cannot be applied to COD testing in the laboratory, because it does not meet the accuracy requirements. This is due to the difference in composition between the COD reagent in the standard method and the COD ready stock

reagent issued by the factory that manufactures COD-meter rapid test equipment, Lovibond. HR reagent in the standard method for the COD value range is 100-900 mg / L, while the COD-meter rapid test method consists of reagent LR 0-150 mg / L, MR 0-1500 mg / L and HR 0-15000 mg / L and special measurement features are designed according to the reagent range used.

Table 4. Z-score in various methods

C_{CRM}	Metode	C_m	Z- score
8000 ± 68	M1-LR	7863,07	0,4
8000 ± 68	M1-HR	7978,35	0,1
8000 ± 68	M2-LR	8064,29	0,2
8000 ± 68	M2-HR	8027,14	0,1
8000 ± 68	M3-LR	7842,86	0,5
8000 ± 68	M3-HR	7533,57	1,5
8000 ± 68	M4-LR	7986,42	0,0
8000 ± 68	M4-HR	8100,40	0,3

Another statistical method used to evaluate the performance of the method is through the Z-score test according to equation (8) and (9) [10][11]. From the Z-score test results for each method in Table 4 gives a value smaller than 2, which means that all methods provide satisfactory performance. However, the M3 method for HR gives the highest Z-score value of 1.5, which is also in accordance with the results of a comparison test with the CRM values discussed earlier. This further reinforces that the M3 method is not applicable as a testing method in the laboratory

CONCLUSION

The Rapid Test Method COD Vario Lovibond (M1) method gives satisfactory results like the standard method APHA (M2), so it recommends as a companion method to the standard method.

LPT-FMIPA can submit additional accredited scopes to the National Accreditation Agency (KAN) for COD testing parameters using the standard method and Rapid test COD-Vario Lovibond method by attaching documents resulting from APHA standard method verification and validation of the Rapid test COD-Vario Lovibond method.

ACKNOWLEDGMENT

The authors grateful to Research Centre Unsri for funding educational research scheme DIPA in 2019 (Contract No. 0148.04/UN9/SB3.LP2M.PT/2019). Also special thank you to Dean of FMIPA who has supported the PLP research.

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