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Research Article

Mercury Determination Using Stannous Chloride Reductant Followed by Atomic Absorption Spectrometric Measurement: Performance Characteristics, Uncertainty Estimation, and Compliance Assessment

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Abstract

Indonesian government has committed to reduce and eliminate mercury. Hence, the intensity of monitoring activities of mercury levels in various matrices would be increased and supported by qualified analytical data. Key characteristic performances, i.e., the limit of detection, linear range, precision, trueness, have been successfully carried out, and the method was shown to fit the purpose. The limit detection, LoD and LoQ, were found to be 0.26 and 0.86 μg/L, respectively, which were adequate to reach the tightest regulatory limit of mercury in surface water (1 μg/L). The examined linearity range of 1-20 μg/L has been found sufficient for its application since a high mercury concentration in the typical sample is seldomly expected. Precision and trueness aspects of the method were shown to have satisfaction performance, with CV of 1,24% and recovery of 104.54%. All the possible uncertainty sources have been identified in this study. Since no reference material was available, the uncertainty of bias was evaluated through the recovery of the spiked sample. Compliance assessment to six measurement results has been performed; one result was below LoQ, four were clearly below regulatory limit, and one was questionable. Hence a decision rule was applied.

Keywords: decision rule, mercury, performance characteristic, uncertainty

1. Introduction

Mercury is a highly toxic element found naturally and anthropogenic in the environment. Natural sources of atmospheric mercury include volcanoes, geologic deposits, and volatilization from the ocean, rocks, sediments, water, and soils. Anthropogenic emissions contain mercury released from fuels or raw materials, or uses in products or industrial processes, and become an environmental problem (Mallongi et al., 2014; Krisnayanti et al., 2012). One of the significant mercury emission sources comes from artisanal small-scale gold mining (ASGM) that uses mercury amalgamation during gold extraction. There are several reports on the negative impact of mercury on the miners in Indonesia (Bose-O'Reilly et al., 2016; Gibb and O-Leary, 2014). Through Presidential Decree No. 21 in 2019 has comitted to conduct national action to reduce and eliminate mercury utilization. Consequently, monitoring activities of mercury levels in various environmental matrices is performed routinely throughout environmental laboratories in the country. Valid analytical laboratory results are the cornerstone to assure the activities' quality and ensure the correct decision-making based on those results.

There is various existing analytical technique such as inductively coupled plasma atomic emission spectroscopy (Fernández et al., 2015), cold vapor atomic fluorescence spectrometry (da Silva et al., 2012; Torres et al., 2015), voltammetry (Gao and Huang, 2013), and cold vapor atomic absorption spectrometry (Al-Meer et al., 2018; Singh et al., 2013). The latest technique is widely used in many analytical laboratories in Indonesia for mercury analysis due to its superior sensitivity and selectivity. This technique employed stannous chloride (Al-Meer et al., 2018; Guevara-Riba et al., 2006) or sodium borohydride (Fernández et al., 2015; Manzoori et al., 1998) as the reductant to reduce the post digestion inorganic mercury into the Hg^o atom, ready to be measured by the atomic absorption instrument. The detection limit of mercury determination using sodium borohydride is relatively high, i.e., LoQ 11 ppb (Koesmawati et al., 2021), which is higher than the regulatory limit of surface water class I of 1 ppb (Indonesian Presidential Decree No. 82 of 2001). Stannous chloride provides better sensitivity and detection than borohydride, as confirmed through this study. Hence it is suitable to analyze low concentration samples like surface water.

Since valid analytical results come from an accurate analytical method, characterizing the method's performance is inevitable. Actual performance should be investigated appropriately, cover the limit of detection (LoD), the limit of quantification (LoQ), linear range, precision, and trueness, to ensure that the method fits its intended use. There are many reports regarding method validation of mercury determination (Torres et al., 2015; Al-Meer et al., 2018).

Uncertainty is a crucial indicator of the quality of analytical results since both random and systematic errors of the analysis are incorporated in the estimation. Uncertainty estimation could be done through bottom-up (Zhu et al., 2015) or the top-down approach (Pereyra et al., 2013), depending on its fitness for purpose. The former is the more exhaustive estimation since it comprises all uncertainty sources of the analytical procedure. Hence it is preferable in the case where analytical results are very closed to limit value, e.q. Regulation limit. The Eurachem Guide guides uncertainty estimation: Quantifying uncertainty in analytical measurement (Ellison et al., 2000).

In this study, an attempt has been made to evaluate the analytical method's performance characteristics of mercury by cold vapor technique using stannous chloride as reductant followed by atomic absorption spectrometric (AAS) measurement. Since no referene material is available, the trueness study was performed through recovery evaluation using spiked samples. Subsequently, its performance will determine its uncertainty, which was estimated according to the bottom-up method. All of the possible sources of tension were explored and identified. The well-characterized analytical method was then implemented to determine the mercury content in surface water samples taken from areas around ASGM activities in Sukabumi, Indonesia. The results were compared to the regulatory limit. Compliance of the results to the limit has been evaluated based on the relevant decision rule.

2. Methods

2.1 Reagents and Instrument

Throughout the study, 5% (w/v) potassium permanganate and 5% (w/v) potassium persulfate and sodium chloride from Merck; hydroxylamine hydrochloride and stannous chloride from Loba Chemie were used. Concentrated nitric (65%), sulphuric acid (98%), and hydrochloric acid (37%) from Merck were used for digestion. A Mercury standard solution of 1,000 mg/L was used to prepare a diluted standard solution for instrument calibration. Millipore water with a conductivity of 16.2 MΩwas used for dilution. The vapor generator accessories and Agilent Atomic Absorption Spectrometry (AAS) Duo System were used to generate mercury vapor and the samples' spectrometric measurement, respectively.

2.2 Sample Preparation

Samples from Cibareno, Ciletuh, Cimarinjung, and Cikanteh River located around the ASGM activities in Sukabumi, West Java, Indonesia, were collected and used as the matrices sample for the characteristic performance study. Several surface water samples were also taken from the area for analysis. Samples were collected in quartz bottles and preserved using 0.05 N of nitric acid, screw-capped, and stored at 5 °C. Before research, samples were filtered using a Millipore membrane filter of 0.45 µm. Precise volume of 100 mL of sample was pipetted to 250 mL Erlenmeyer flasks, then 5 mL of concentrated sulfuric acid and 2.5 mL of concentrated nitric acid were added. 15 mL of potassium permanganate solution was added to the mixture, let stood for 15 minutes, then heated in the water bath at 95 °C for 2 hours. After cooled to room temperature, the hydroxylamine-hydrochloride solution was added dropwise to reduce the excess of permanganate. Sample solutions then reduce with 25 % (w/v) stannous chloride in an acidic solution to generate the mercury vapor and finally be measured using the atomic absorption instrument. All calibration solutions were treated similarly to the samples.

2.3. Performance Characteristic, Uncertainty, and Implementation of Method

Performance characteristics of an analytical method carried out during the study were included linearity check, the limit of detection, linearity range, precision, and trueness. Linearity check was conducted using a series of various concentrations of calibration solutions. The regression curve was obtained then examined to confirm linearity. LoD and LoQ were determined through several independent measurements of low-level samples and estimated as 3 and 10 times the standard deviation of the replicate measurements, respectively. Method precision and recovery were examined using river water (C_1) spiked with ten µg/L of stock solution (C_2), and the mixture was subjected to the whole analytical protocol and being measured (C_3). The spiked standards (Rec, %) were then calculated using $(C_3-C_1)/C_2$. 100% equation. The variation of results arising random effect of replicate measurements of spiked samples from the same data series provides a suitable basis for precision evaluation.

Estimation of uncertainty was conducted using a bottom-up approach and referred to Eurachem/CITAC Guide: The fitness for the analytical method (Magnusson and Ornemark, 2014). According to the guide, there are five main steps in the uncertainty estimation: 1) confirming specification of the measurand, 2) identifying uncertainty sources, 3) quantification of each uncertainty source, 4) calculating combined uncertainty, 5) calculating expanded uncertainty and reporting.

The verified method was then utilized to determine the mercury content in surface water samples taken from the ASGM area. Analytical results were then compared with the applicable regulatory limit. If results are closed to the regulatory limit, then relevant decision rules need to be implemented to stated compliance with the limit.

3. Result and Discussion

3.1. Stannous Chloride

In mercury analysis using cold vapor AAS, inorganic mercury in the digested sample should be converted into the Hg^o atoms. The Hg^o atoms are in a vapor state that could be conveniently purged into the quartz-ended tube cell placed in the AAS instrument with the assistance of inert gas flow (i.e., argon gas). The atoms are then ready to absorb the mercury analytical line of 253.7 nm emitted from the mercury hollow cathode lamp.

The efficiency of the reductant to formed Hg^o atoms is essential since it will determine the sensitivity and detection limit of the analytical method. The selection of the reductant should consider the fitness of the analytical method. In this study, the objective was to evaluate whether the samples collected from rivers in Sukabumi have complied with the regulatory limit for mercury in surface water (the highest limit is 1 ug/L). Therefore, the analytical detection limit should be meet the regulatory level. Stannous chloride is a suitable reductant for this purpose, as confirmed by this study.

3.2. Performance Characteristics

Linearity check was conducted using a series of various concentrations of calibration solutions of 1, 5, 10, 15, 20 µg/L. The results are presented in Table 1. The range of concentration standards that have been examined was relatively broad, i.e., between 1-20 µg/L. This range was still possible to be expanded since the absorbent for 20 µg/L was still at the level around 0.27, which was far from the typical saturated absorbance level in atomic spectrometry measurement of 0.8 (Agilent user manual, 2017).

Table 1. Experimental results for linearity range check of the calibration curve

Conc. of Standard (ug/L)	Yi	Yc	Residue (Yi-Yc)	Slope	Intercept	Correlation Coefficient (R)
0	0	-0.002037	0.002037	0.0136455	-0.00204	0.99976921
1	0.0114	0.011609	-0.000209			
5	0.0639	0.066191	-0.002291			
10	0.1324	0.134418	-0.002018			
15	0.2062	0.202646	0.003554			
20	0.2698	0.270873	-0.001073			

However, considering that the method is intended to be applied to the surface water (river, lake, aquifer), a high mercury level is rarely expected. The examined range in this study was considered adequate for its intended purpose. As presented in Table 1, the correlation coefficient of the regression curve was excellent; however, to confirm linearity, the data were further processed to obtain the residual values (difference of actual absorbance value (Yi) and the theoretical value obtained from the regression equation (Yc)). The graphical plot of the residues (Figure 1) confirmed no significant systematic trend of the curve. Hence linearity of the curve up to 20 µg/L was confirmed.

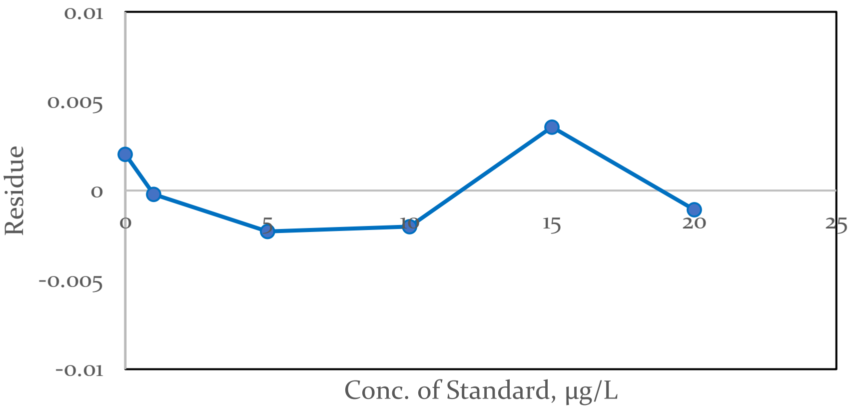

Figure 1. Graphical plot of the residues, no systematic trend was observed

LoD and LoQ were determined through replicate measurements of low concentration samples using whole analytical protocol; the results are tabulated in Table 2. A natural sample with a low mercury level was perfect for determining the detection limit since it consists of various matrices naturally existing in typical samples. Its concentration was low enough to represent the variation of low-level measurements. As presented in the left side of Table 2, the LoD and LoQ were both below the tightest regulatory limit for surface water class I of 1.0 µg/L. Hence, the fitness for this method has been confirmed concerning the level of the detection limit.

Table 2. Experimental results for determination of detection limit (left), and precision & recovery (right)

Sample code	**Abs**	**Conc. (µg/L)**	**Sample Code**	**Abs**	**Spiked Sample, C_3 (µg/L)**	**Rec (%)**
S1	0.0046	0.4853	SS1	0.1439	10.7279	103.37
S2	0.0047	0.4926	SS2	0.1431	10.6691	102.78
S3	0.0045	0.4779	SS3	0.1452	10.826	104.35
S4	0.0044	0.4681	SS4	0.1441	10.7451	103.54
S5	0.0024	0.3211	SS5	0.1451	10.8186	104.28
S6	0.0024	0.3211	SS6	0.1475	10.9951	106.04
S7	0.0024	0.3260	SS7	0.1478	11.0172	106.27
S8	0.0022	0.3088	SS8	0.1474	10.9853	105.95
S9	0.0023	0.3162				
Average		0.3908	Average		10.85	104.57
Standard deviation, s		00859	s		0.13	1.35
LoD		0.258	CV (%)		1.24	1.29
LoQ		0.859				

The experiment for precision and recovery characterization has been set up efficiently, as seen on the right side of Table 2. From the same experiment, two performance characteristics, i.e., precision and recovery, could be evaluated. Accuracy of the method has been performed within one laboratory with the same personnel, using the same instrument, and within a short period. Hence, the repeatability precision was obtained—the coefficient of variation of 1.24% was much lower than the standard reference of 2/3.$CV_{Horwitz}$ (29.2%), hence, the repeatability of the method was considered relatively good. Similarly, the average recovery was found to be 104.57% that was a typical recovery value at this level (ppb). Recovery values more significant than 100% were not uncommon for the analytical method, as reported by several studies (Maxwell et al., 1993 and Hseu et al., 2004). It is also relatively good compared to the AOAC reference of 60-120% for ppb level (Paez et al., 2016).

3.3. Estimation of Uncertainty

In this study, uncertainty estimation was applied to the measurement of six surface water samples; the results are summarized in Table 3. There was 1 sample giving a result below LoQ, hence excluded from uncertainty estimation.

3.3.1 Specification of the Measurand

Measurand is the quantity intended to be measured; in chemistry, "analyte" is sometimes used for "measurand" (International vocabulary metrology (VIM), 2008). The first step carried out in uncertainty estimation was to specify the measurand to understand what is being measured fully, the overall analytical procedure, and how the measurand was calculated. Mercury concentration in the samples has been determined using the cold vapor AAS technique using the following equation

$$C_S = C_x \cdot \frac{100}{Rec} \tag{1}$$

Where Cs = mercury concentration in the sample, Cx = mercury concentration in the measured sample solution, Rec = recovery of the method.

Table 3. Summarized results fo surface water samples

Sample Code	Vsample (mL)	Abs	Cx (µg/L)	Rec (%)	Cs (µg/L)
SW1	100	0.0255	2.1013	104.57	2.0095
SW2	100	0.0131	1.1985	104.57	1.1461
SW3	100	0.0304	2.4555	104.57	2.3482
SW4	100	0.4244	3.3342	104.57	3.1885
SW5	100	0.0672	5.137	104.57	4.9125
SW6	100	0.0019	0.3795	104.57	<LoQ *

*LoQ = 0.86 µg/L

3.3.2 Identification of Uncertainty Sources

The next step was to identify all of the sources of uncertainty. Each of the parameters stated in the equation to get the result (Eq. 1) has its intrinsic uncertainty. Hence they were all identified as primary sources, namely Cx (concentration of the measured sample, obtained from calibration curve) and Rec (recovery of method). Another parameter that did not explicitly exist in Eq. 1, but was considered to contribute to overall uncertainty arose from the standard solution. There were two components, i.e., delay from the stock mercury standard solution and the random error arising from the preparation of the serial calibration standards through volumetric dilution. Another essential source arises from the repeatability of the method (Rep) since this was a measure of random effect from replicating the whole procedure. All identified sources of uncertainties were systematically presented in the fishbone diagram (Fig 3.)

A factor of volume of reagents and reductant was not considered uncertainty sources since the method must be stated in an excessive amount. Similarly, time and temperature were also parameters that were not rigidly followed along with the procedure. Hence the loose variation of that condition will not have much effect on the result. Instrument instability, for sure, would give a specific contribution to the overall uncertainty. However, it was already taken into account in the Cx.

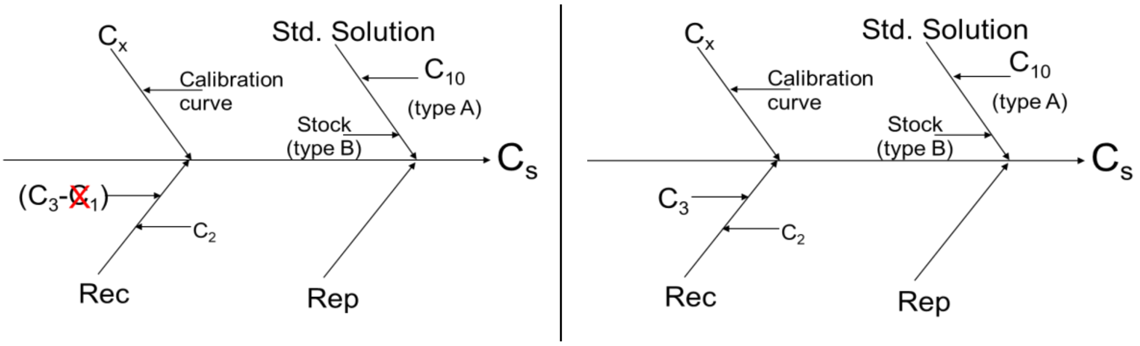

Figure 2. Fishbone diagram describing uncertainty sources: before (left) and after revised (right)

Laboratory personnel who performed the measurement is undoubted will contribute to the overall uncertainty of the result. The coefficient of variance (CV) obtained from replicate measurements performed by less trained personnel will be relatively more significant than those obtained from well-trained personnel. In addition, this contribution is typically much more extensive than those arising from instrument calibration or standard solution concentration. Therefore, personnel commonly consider as primary uncertainty sources. In this study, uncertainty arising from personnel was taken into account in the precision parameter (Rep). Delay arises from method recovery was estimated based on the equation Rec = $(C_3\text{-}C_1)/C_2$. 100%, hence the components of uncertainties were put in the diagram (bottom part of the left diagram). However, the concentration of samples, C_1, was estimated from the standard deviation from replicate measurements of samples and method repeatability (Rep). Therefore, the C1 was eliminated from the diagram to avoid double-counting, as seen in the revised diagram (suitable side diagram of Fig. 2).

3.3.3. Quantifying Uncertainty Sources

The purpose of the third step was to quantify all uncertainty sources identified in the previous step. Uncertainty arises from Cx was evaluated from the data series of the calibration solutions, i.e., 1, 5, 10, 15, 20 μg/L, each was measured in triplicate. The standard deviation of the curve, $S_{Y/X}$, was a measure of the variation of the residues (difference between actual absorbance being measured with the theoretical value according to regression line) and could be calculated using Eq. 2, where Yi = absorbance of the calibration solutions, Yc = theoretical value of absorbance according to the regression line, and n = number of measurements.

$$S_{Y/X} = \sqrt{\frac{\Sigma(Yi-Yc)^2}{(n-2)}} \tag{2}$$

Afterward, the uncertainty of the concentration of a measured solution, $\mu(C_X)$, was calculated using Eq. 3, taking into account the absorbance value of the sample.

$$\mu(C_X) = \frac{S_{Y/X}}{b}\sqrt{\frac{1}{m}+\frac{1}{n}+\frac{\left(Y_{Spl}-Y_{mean}\right)^2}{b^2.\ \Sigma(X_i-X_{mean})^2}} \tag{3}$$

In Eq. 3, $\mu(C_X)$ = uncertainty of concentration of sample solution, b = slope of the regression line, m = number of replication of sample measurements, n = number of calibration solution, Y_{Spl} = absorbance of sample, Y_{mean} = mean of absorbance of standards, X_{mean} = means of concentration of standards. A spreadsheet calculation has been made to performed measures using Eq. 3 and 4, as presented in table 4.

Uncertainty arises from precision was estimated using repeatability of method, represented by CV of 1,24%, and directly taken as relative standard uncertainty, ready to be combined with other uncertainty components.

There were two sources of uncertainty arises from the standard solution, i.e., stock-standard solution, and C10, a calibration solution representing the random error of serial dilution of five calibration solutions. Uncertainty of stock standard solution was estimated from 1,000 (2 mg/L (95% confidence level) certificate. Since it is classified as type B, the standard uncertainty was easily calculated as 2/2 = 1 mg/L.

Table 4. Spreadsheet calculation to obtain $S_{Y/X}$ and $\mu(C_X)$

No	Xi	Yi	Yc	$(Yi-Yc)^2$	$(Xi-Xmean)^2$
1	1	0.0114	0.0104	0.000001	84.6
2	1	0.0112	0.0104	0.000001	84.6
3	1	0.0116	0.0104	0.000002	84.6
4	5	0.0639	0.0653	0.000002	27.0
5	5	0.0641	0.0653	0.000001	27.0
6	5	0.0637	0.0653	0.000003	27.0
7	10	0.1324	0.1340	0.000003	0.0
8	10	0.1321	0.1340	0.000004	0.0
9	10	0.1327	0.1340	0.000002	0.0
10	15	0.2062	0.2027	0.000012	23.0
11	15	0.2058	0.2027	0.000010	23.0
12	15	0.2066	0.2027	0.000015	23.0
13	20	0.2698	0.2713	0.000002	96.0
14	20	0.2703	0.2713	0.000001	96.0
15	20	0.2693	0.2713	0.000004	96.0

No	Xi	Yi	Yc	$(Yi-Yc)^2$	$(Xi-Xmean)^2$
Mean	10.2	0.13674			
Sum	153			6.251E-05	692.4
n	15				
Sy/x	0.0022				
u (Cx)	0.1341	ug/L			

The uncertainty evaluation of the C10 calibration standard was relatively exhaustive, since there were multiple dilution step have been taken to come from 1,000 mg/L to 10 µg/L, according to Eq. 4,

$$C_{10} = C_{1000}\,\frac{V_1}{V_{100}} \cdot \frac{V_1}{V_{100}} \cdot \frac{V_{10}}{V_{100}} \tag{4}$$

where C10 = standard concentration of 10 µg/L, V1 = volume of pipette of 1 mL, V10 = volume of pipette of 10 mL, V100 = volume of volumetric flask of 100 mL. The uncertainty of C10 was then calculated using equation 5, where µ(C10), µ(C1000), µ(V1), µ(V10), µ(V100), were the standard uncertainty of C10, C1000, V1, V10, and V100, respectively.

$$\mu(C_{10}) = C_{10}\sqrt{\left(\frac{\mu(C_{1000})}{C_{1000}}\right)^2 + 2.\left(\frac{\mu(V_1}{V_1}\right)^2 + \left(\frac{\mu(V_{10}}{V_{10}}\right)^2 + 3.\left(\frac{\mu(V_{100}}{V_{100}}\right)^2} \tag{5}$$

Given that the standard uncertainty of C1000, V1, V10, and V100 are 2 mg/L, 0.0012 mL, 0.068 mL, and 0.0682 mL, respectively, the delay of C10 was easily calculated using Eq. 5 and obtained the value of 0.0208 µg/L. Since C10 represented five calibration solutions, the matter was divided by 5, hence 0.0208/5 = 0.0042 µg/L.

Since the recovery was calculated as $(C_3-C_1)/C_2$. 100%, then the uncertainty that arises from recovery was calculated according to Eq. 6. Please note that the fate of C2 was eliminated due to the double-counting effect, as described in the revised fishbone diagram (Fig. 2).

$$\mu(Rec) = Rec\sqrt{\left(\frac{\mu(C_3}{C_3}\right)^2 + \left(\frac{\mu(C_2}{C_2}\right)^2} \tag{6}$$

The value of Rec, C3, and C2 were 104.57%, 10.85 µg/L, and 10 µg/L, respectively. The standard uncertainty of C3 was estimated from the standard deviation of replicate measurements of spiked solutions of 0.13/√6 = 0.053 µg/L, while the standard delay of C2 has already been calculated previously, i.e., 0.0208 µg/L. Hence, calculated using Eq. 6, the µ(Rec) was found to be 0.556%.

3.3.4. Combined Uncertainty

The fourth step was to combine all of the uncertainty sources concerning the relevant combination rule described in the Eurachem guide: The use of expanded uncertainty information in compliance assessment (Ellison and Williams, 2007). The recapitulation is presented in Table 5 showed the combined standard uncertainty of C_S found to be 0.127 µg/L. The rank given in the right column were indicated the relative contribution of each component. It was found that C_X was the biggest, continue by Rep, Rec, stock, and C10. Since the C_X concentration of the measured sample was the biggest, one should give close attention to the quality of the calibration curve to control the uncertainty.

3.3.5. Calculation of Expanded Uncertainty, Report, and Evaluation of Results

An expanded uncertainty value was calculated as $U(C_S) = k.\ \mu_C(C_S)$, where k is the coverage factor usually taken as 2 for 95% confidence level if the number of data (hence, the degree of freedom) is large enough. If the degree of freedom is low, then k is taken from the corresponding t-student's value. In this study, k was taken as 2. Hence the expanded uncertainty, $U(C_S)$, was found to be 0.2542 µg/L for SW1. Since the delay should not report more than 2 significant figures, the analysis results of mercury concentration in a surface water sample with its expanded uncertainty are 2.01 ± 0.25 μg/L, with 95% confidence level.

Table 5. Recapitulation of combined standard uncertainty

Uncertainty Source	Value (X)	Standard Uncertainty (μ_X)	Unit	(μ_X/X)	Rank
C_X	2.1013	0.1298	μg/L	0.061786	1
Rep	-	-	-	0.012400	2
Rec	104.57	0.556	%	0.005315	3
Stock, Type B	1000	1	μg/L	0.001000	4
C_{10}, Type A	10	0.00416	μg/L	0.000416	5
C_S	2.0095	0.127	μg/L		

Table 6. Summary of measurement results and their uncertainties

Sample Code	Cs, μg/L	μ(Cs), μg/L	k	U(Cs), μg/L	Rel. Std Unc. (%)	2/3 $CV_{Horwitz}$ (%)	Reg. Limit μg/L
SW1	2.01	0.13	2	0.26	6.47	27.2	5.0
SW2	1.15	0.13	2	0.26	11.34	29.6	5.0
SW3	2.35	0.13	2	0.26	5.54	26.5	5.0
SW4	3.19	0.13	2	0.26	4.08	25.3	5.0
SW5	4.91	0.14	2	0.28	2.85	23.7	5.0
SW6	<LoQ *	N/A	N/A	N/A	N/A	N/A	5.0

*LoQ = 0.86 μg/L

The relative standard uncertainty was 6.33%, which was lower than the standard limit of 2/3.$CV_{Horwitz}$ of 27.16% indicated that the estimation was entirely rational. Summary of all measured samples and their uncertainties are given in Table 6.

All of the uncertainties of the results were far below the standard reference of 2/3 $CV_{Horwitz}$, confirming that the estimation had naturally been performed, except for SW6. The delay could not be performed since the result was below the limit detection. The Indonesian Presidential Decree gave regulation for surface water No 82 in 2001, stating that mercury limit was 1, 2, 2, and 5 μg/L for class I, II, III, and IV of surface water, respectively. Compared to this value, the results of SW1, SW2, SW3, SW4 with its uncertainty were clearly below the limit of water Class IV. Hence the quality of compliance assessments was high. However, for SW5, the result was slightly below the limit. If expanded uncertainty is considered, there would be a questionable situation since some part of the result was below the limit. In contrast, the other part was upper the limit. The condition of all results for decision-making is illustrated in Fig. 3.

To resolve the situation, a clear decision rule is needed. The decision rule describes how measurement uncertainty is accounted for when stating compliance with a specified requirement (ISO/IEC 17025, 2017). Ideally, the decision rule is providing by the regulator. However, it was not the case. Hence, a decision rule that was considered to be relevant was employed, i.e., Eurachem/CITAC Guide (Ellison and Williams, 2007). In this case, the decision-making has been made at 95% confidence level. Hence the guard band for the decision has been set as 1.65. $\mu(C_S)$ = 1.65 . 0.14 = 0.23 μg/L. The decision limit was then calculated as 5-0.23 = 4.77 μg/L. All results below the value would be accepted, while results equal or above the value would be rejected. Since the result was 4.91, which was greater than the decision limit value, it was rejected, meaning that the SW5 did not comply with the regulatory limit.

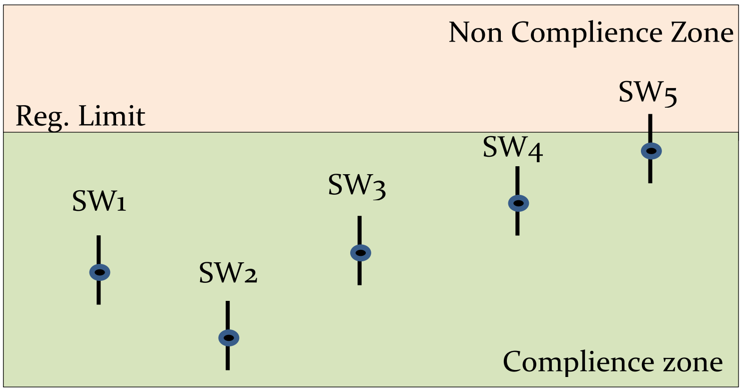

Figure 3. Illustration of the situation for compliance assessment of analytical results

4. Conclusions

Method for determining mercury using stannous chloride as reductant followed by absorption spectrometric measurement has been successfully characterized for its performances. Key characteristic performances, i.e., the limit of detection, linear range, precision, trueness, have been successfully carried out, and the method was shown to fit its intended purpose.

Uncertainty of the measurement results was successfully estimated using a bottom-up approach. All of the possible uncertainty sources have been identified. Although not included in the equation of measurand, uncertainty arising from standard solution has been properly incorporated in the estimation. Delay arises from method recovery, although approached through analysis of the spiked sample, has been adequately estimated. However, to better measure the bias, the use of suitable certified reference material in the trueness study is recommended.

Compliance assessment was performed to the results. Out of six samples, one sample was questionable. Hence, a clear compliance statement could not be demonstrated. Since the regulator did not provide a suitable decision rule, the existing guide from Eurachem has been applied and found to resolve the problem successfully. However, it is recommended that the regulator become aware of the need for a clear guide for compliance assessment of analytical results and publish the relevant decision rule as soon as possible.

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