Assigned value determination by expert laboratory consensus on heavy metals proficiency testing of environmental laboratory 2018

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Abstract. Determination of assigned values is an important stage in proficiency testing schemes in accordance with SNI / ISO 17043: 2010. Assigned value is a reference for determining the laboratory performance status in proficiency test participants. One alternative in determining Assigned value is through expert laboratory consensus. This method has an advantage over the reference value method, namely when there is no certificate reference material (CRM) that matches the proficiency test commodity or the corresponding CRM value is not in place. This study was aimed at determining the assigned value of laboratory proficiency testing of heavy metal parameters by employing the expert laboratory consensus method. In this study, the expert laboratory tested were 20 laboratories included the one in the environmental metrology road map. The laboratories have been accredited according to ISO / IEC 17025. Statistical calculations through Algorithm A, and iteration technique were implemented in this procedure. This will make it easier to determine the assigned value because it does not need to be through the reference value calibration of the CRM value. It was found out that the assigned value in mg/L for each metal, i.e Zn, Fe, Mn and Cd were 0.08; 0.4; 0.3 and 0.06 respectively. It was also shown that the assigned value derived from this expert laboratory consensus were not significantly different from the target value, except for Zn metal that differed from the target by 0.01 mg/L. However, it is important to keep reviewing the competence of the expert laboratory on a regular basis to ensure the validity of the values produced.

1. Introduction
Protection and management of the environment as mandated in the Law of the Republic of Indonesia No. 32 of 2009 will be effective and efficient if supported by data produced by competent environmental laboratories [1]. To find out the competency of an environmental laboratory, a proficiency test program is needed.

Proficiency testing is one method to find out the performance of a laboratory by means of an inter-laboratory comparative test. The purpose of the proficiency test program is to thoroughly check the technical performance in a laboratory [2, 3]. Distilled water mixed with certain amount of standard solution was used in this experiment. Water sample was the most frequently characterized product and commonly applied as key parameters [4]. Water quality testing is also the most common procedures used in laboratories. The evaluation result obtained further can be used to identify laboratory competencies in testing certain parameters [5]. Center for Research and Development of
Quality and Environmental Laboratory of Research, Development and Innovation Agency of Ministry of Environment and Forestry (P3KLL) applies a proficiency test program policy to see traceability of a given laboratory measurements (tests) and as an evaluation material, to determine the performance of environmental laboratories in Indonesia [6].

The proficiency test of the environmental laboratory carried out in the study, refers to SNI ISO/IEC 17043: 2010 concerning the conformity assessment of the general requirements for proficiency testing [7]. The evaluation method used in data processing refers to ISO 13528: 2015 concerning statistical methods for use in proficiency testing by inter-laboratory comparison. Data evaluation was conducted to determine the performance of each participant's laboratory.

2. Methodology
The implementation of proficiency test programs is carried out annually with the scope of testing the environmental quality parameters based on quality standards in accordance with environmental legislation. The samples were distributed to 100 laboratories across Indonesia. Twenty two (22) of them were chosen as part of metrology road map [8]. In the future, the laboratories are expected to become the expert laboratories. The laboratories are belonging to governmental institutions and encompassing various sectors such as food, industry, health, public works and environment.

2.1. Material
The samples distributed to the participants were distilled water mixed with certain amount of standard solution of Zn, Cd, Fe and Mn. The materials used in the preparation of solutions for the proficiency analysis of heavy metals parameters in water were the stock standard solution of Zn, Cd, Fe and Mn, 1000 mg/L respectively, concentrated supra-pure 65% HNO3 and aquadest. The apparatus used in the preparation work were 50 L containers, 2 L measuring flask, measuring pipettes, and Flame Atomic Absorption Spectrophotometer (FAAS). Summary of material, procedure and assigned target value applied in this research is presented in table 1.

2.2. Procedure
Each participant's laboratory was given a laboratory code number. The provision of this code aimed to maintain the confidentiality of the test results reported to the organizer and the results of evaluations reported to participants. The target value and the method used in determination are as reported below [9-12].

| No | Testing Parameter | Unit | Method | Target value concentration |
|----|-------------------|------|--------|----------------------------|
| 1  | Fe                | mg/L | APHA 3111A-2017/AAS Flame | 0.40                      |
| 2  | Mn                | mg/L | APHA 3111A-2017/AAS Flame | 0.30                      |
| 3  | Cd                | mg/L | APHA 3111A-2017/AAS Flame | 0.06                      |
| 4  | Zn                | mg/L | APHA 3111A-2017/AAS Flame | 0.08                      |

The stages of proficiency test preparation include:

- Determination of samples to be tested covering types of test sample, types of analytes/test parameters, concentration of each analyte in the test sample, i.e. Zn, Fe, Mn and Cd, and determination of target value, which was adjusted to Government Regulation No. 82/2001, concerning management of water quality and control of water pollution [13].
- Homogeneity and stability test.
• Assigned value determination.
• Distribution of proficiency test samples to participant laboratories.
• Collection, verification and evaluation of test results data from participant laboratories.
• Report distribution to the participants and related environmental laboratory development agencies.

2.3 Assigned value determination methods
As mentioned in ISO 13528:2015 concerning statistical methods for use in proficiency testing by inter-laboratory comparison, the assigned value can be determined by five different methods [14, 15]. Certified references material (CRM) are the key points to compare the measurement result providing their traceability [16]. In this paper, the expert laboratories consensus was used to determine the assigned value, while P3KLL as the organizer used the results from one laboratory method to define assigned value [17].

2.3.1 Consensus value from expert laboratory
Using the Algorithm A iteration technique, a robust average and standard deviation from the expert laboratories data were settled. The Algorithm A is an analysis technique that is independent to outliers and applicable to contaminated population. This Algorithm procedure gives robust estimates of mean \((x^*)\) and standard deviation \((s^*)\) from the data that are used as assigned value and standard deviation of proficiency assessment. Iterative calculations was used to update the \(x^*\) and \(s^*\) several times until there is no significant changes in the 3rd significant figure.

As stated in Annex C ISO 13528:2015 [14], steps of Algorithm A iteration technique are described below.

- Determination of initial values of \(x^*\) and \(s^*
Data should be sorted from the smallest to the largest. The robust mean value and the standard robust deviation value are denoted by \(x^*\) and \(s^*\) respectively. As the initial value \(x^*\) the median value is taken from the data, while the value \(s^*\) is derived from the formula:

\[
s^* = 1.483 \times \text{med I}\ x_i - x^*\ I
\]

Remarks:

- \(\text{Med I}\) = median
- \(x_i\) = value of the test results of participants
- \(x^*\) = robust mean value (in the initial stage calculated from the median of all participant data)

- Calculation of the limit (\(\delta\))

\[
\delta = 1.5 \times s^*
\]

From the above calculation, if the data at the top \((x_1, x_2\text{ etc.})\) is less than \(x^* - \delta\), then the value of \(x_1\) is replaced by the value \(x^* - \delta\). If the data at the bottom \((x_n, x_{n-1}\text{ etc.}) > x^* + \delta\), then the value of \(x_n\) is replaced by the value \(x^* + \delta\). This process should be repeated until the data converges which is when the values of \(x^*\) and \(s^*\) do not change to 3rd significant numbers. The \(x^*\) value of the converged data is the assigned value of the robust mean and \(s^*\) is the robust standard deviation.

- Uncertainty of the assigned value is determined using the formula below [18].
\[ \mu x = 1.25 \times s^* / \sqrt{p} \]  \hspace{1cm} (3)

Remarks:
\[ \mu x = \text{uncertainty of assigned value} \]
\[ P = \text{number of participants} \]

2.3.2 Results from one laboratory
The next procedure, on the other hand, the assigned value determination in P3KLL laboratory using results from a calibration against the reference values of a closely matched certified CRM [18]. While in this research, we tried a different way in determining assigned value that does not require calibration. This method used the statistic in ISO 13528 Annex C, Algorithm A iteration calculation.

3. Result and Discussion
The assigned value determination, Algorithm A and iterative calculation for each element of heavy metals are shown below. In the case of Fe, the data are presented in table 2.

| Iteration | 0 | 0.078 | 0.078 | 0.078 |
|-----------|---|--------|--------|--------|
| d = 1.5 x* | --- | 0.322 | 0.330 | 0.330 |
| x* - d | --- | 0.478 | 0.487 | 0.487 |
| x* + d | --- | 0.322 | 0.330 | 0.33 |
| L-062 | 0.312 | 0.088 | 0.322 | 0.330 |
| L-044 | 0.345 | 0.055 | 0.345 | 0.345 |
| L-025 | 0.360 | 0.040 | 0.360 | 0.360 |
| L-049 | 0.36 | 0.040 | 0.360 | 0.360 |
| L-010 | 0.37 | 0.030 | 0.370 | 0.370 |
| L-076 | 0.389 | 0.011 | 0.389 | 0.389 |
| L-081 | 0.39 | 0.010 | 0.390 | 0.390 |
| L-098 | 0.390 | 0.010 | 0.390 | 0.390 |
| L-007 | 0.396 | 0.004 | 0.396 | 0.396 |
| L-045 | 0.40 | 0.000 | 0.400 | 0.400 |
| L-078 | 0.400 | 0.000 | 0.400 | 0.400 |
| L-031 | 0.41 | 0.010 | 0.410 | 0.410 |
| L-054 | 0.412 | 0.012 | 0.412 | 0.412 |
| L-092 | 0.429 | 0.029 | 0.429 | 0.429 |
| L-026 | 0.447 | 0.047 | 0.447 | 0.447 |
| L-073 | 0.456 | 0.056 | 0.456 | 0.456 |
| L-059 | 0.46 | 0.060 | 0.460 | 0.460 |
| L-091 | 0.481 | 0.081 | 0.478 | 0.481 |
| L-088 | 0.52 | 0.120 | 0.478 | 0.487 |
| L-077 | 0.524 | 0.124 | 0.478 | 0.487 |
| AVERAGE | | 0.41255 | | |
| SD | | 0.06 | | |
| New x* | | 0.400 | | |
The assigned value determination, Algorithm A and iterative calculation for Mn are described as shown in table 3.

### Table 3. Algorithm A, iterative calculation of Mn.

| Iteration | 0  | xᵢ - x* | 1  | 2  | 3  | 4  |
|-----------|----|----------|----|----|----|----|
| d = 1.5 s* | --- | 0.038   | 0.036 | 0.034 | 0.035|
| x* - d    | --- | 0.271   | 0.272 | 0.273 | 0.273|
| x* + d    | --- | 0.347   | 0.343 | 0.342 | 0.343|
| L-044     | 0.145 | 0.164   | 0.271 | 0.272 | 0.273 | 0.273|
| L-062     | 0.191 | 0.118   | 0.271 | 0.272 | 0.273 | 0.273|
| L-091     | 0.229 | 0.080   | 0.271 | 0.272 | 0.273 | 0.273|
| L-098     | 0.289 | 0.020   | 0.289 | 0.289 | 0.289 | 0.289|
| L-007     | 0.292 | 0.017   | 0.292 | 0.292 | 0.292 | 0.292|
| L-076     | 0.295 | 0.014   | 0.295 | 0.295 | 0.295 | 0.295|
| L-045     | 0.30  | 0.009   | 0.300 | 0.300 | 0.300 | 0.300|
| L-073     | 0.306 | 0.003   | 0.306 | 0.306 | 0.306 | 0.306|
| L-078     | 0.306 | 0.003   | 0.306 | 0.306 | 0.306 | 0.306|
| L-077     | 0.308 | 0.001   | 0.308 | 0.308 | 0.308 | 0.308|
| L-049     | 0.31  | 0.001   | 0.310 | 0.310 | 0.310 | 0.310|
| L-081     | 0.31  | 0.001   | 0.310 | 0.310 | 0.310 | 0.310|
| L-088     | 0.31  | 0.001   | 0.310 | 0.310 | 0.310 | 0.310|
| L-010     | 0.32  | 0.011   | 0.320 | 0.320 | 0.320 | 0.320|
| L-054     | 0.326 | 0.017   | 0.326 | 0.326 | 0.326 | 0.326|
| L-092     | 0.329 | 0.020   | 0.329 | 0.329 | 0.329 | 0.329|
| L-031     | 0.33  | 0.021   | 0.330 | 0.330 | 0.330 | 0.330|
| L-059     | 0.33  | 0.021   | 0.330 | 0.330 | 0.330 | 0.330|
| L-025     | 0.335 | 0.026   | 0.335 | 0.335 | 0.335 | 0.335|
| L-026     | 0.338 | 0.029   | 0.338 | 0.338 | 0.338 | 0.338|
| AVERAGE   | 0.29495 |       |       |       |       |       |
| SD        | 0.05 | --      |       |       |       |       |
| New x*    | 0.309 | --      | 0.307 | 0.307 | 0.308 | 0.308|
| New s*    | 0.03  | --      | 0.024 | 0.023 | 0.023 | 0.023|
| Median of x*-x | -- | 0.02 | -- |       |       |       |

The assigned value determination, Algorithm A and iterative calculation for Cd are described as shown in table 4.
Table 4. Algorithm A, iterative calculation of Cd.

| Iteration | 0 | 1 | 2 | 3 |
|-----------|---|---|---|---|
| \(d = 1.5x^*\) | --- | 0.004 | 0.01 | 0.01 |
| \(x^*-d\) | --- | 0.056 | 0.05 | 0.05 |
| \(x^*+d\) | --- | 0.064 | 0.0647 | 0.07 |
| L-062 | 0.047 | 0.013 | 0.056 | 0.05 | 0.05 |
| L-059 | 0.05 | 0.010 | 0.056 | 0.05 | 0.05 |
| L-088 | 0.05 | 0.010 | 0.056 | 0.050 | 0.050 |
| L-077 | 0.052 | 0.008 | 0.056 | 0.052 | 0.052 |
| L-026 | 0.056 | 0.004 | 0.056 | 0.0560 | 0.056 |
| L-098 | 0.057 | 0.003 | 0.057 | 0.057 | 0.057 |
| L-092 | 0.058 | 0.002 | 0.058 | 0.0580 | 0.058 |
| L-078 | 0.0590 | 0.001 | 0.0590 | 0.059 | 0.0590 |
| L-010 | 0.06 | 0.000 | 0.06 | 0.0600 | 0.06 |
| L-031 | 0.06 | 0.000 | 0.06 | 0.06 | 0.06 |
| L-045 | 0.06 | 0.000 | 0.06 | 0.0600 | 0.06 |
| L-049 | 0.06 | 0.000 | 0.06 | 0.06 | 0.06 |
| L-081 | 0.06 | 0.000 | 0.06 | 0.06 | 0.06 |
| L-044 | 0.061 | 0.001 | 0.061 | 0.061 | 0.061 |
| L-007 | 0.0610 | 0.001 | 0.0610 | 0.061 | 0.0610 |
| L-073 | 0.062 | 0.002 | 0.062 | 0.0620 | 0.062 |
| L-054 | 0.073 | 0.013 | 0.064 | 0.0647 | 0.07 |
| L-025 | 0.079 | 0.019 | 0.064 | 0.0647 | 0.07 |
| L-076 | 0.604 | 0.544 | 0.604 | 0.6047 | 0.07 |
| Average | 0.09 | -- | 0.059 | 0.059 | 0.059 |
| SD | 0.13 | -- | | |
| New \(x^*\) | 0.060 | -- | 0.059 | 0.059 | 0.059 |
| New \(s^*\) | 0.003 | -- | 0.004 | 0.005 | 0.005 |

The assigned value determination, Algorithm A and iterative calculation for Zn are described as shown in table 5.

Table 5. Algorithm A, iterative calculation of Zn.

| Iteration | 0 | 1 | 2 | 3 | 6 | 7 | 8 |
|-----------|---|---|---|---|---|---|---|
| \(d = 1.5s^*\) | --- | 0.0240 | 0.0277 | 0.0309 | 0.0351 | 0.0353 | 0.0353 |
| \(x^*-d\) | --- | 0.0580 | 0.0539 | 0.0506 | 0.0468 | 0.0467 | 0.0466 |
| \(x^*+d\) | --- | 0.1060 | 0.1093 | 0.1124 | 0.1169 | 0.1172 | 0.1173 |
| L-045 | 0.05 | 0.032 | 0.0580 | 0.0539 | 0.0506 | 0.05 | 0.0500 | 0.05 |
| L-088 | 0.05 | 0.032 | 0.0580 | 0.0539 | 0.0506 | 0.05 | 0.0500 | 0.05 |
| L-044 | 0.051 | 0.031 | 0.0580 | 0.0539 | 0.0510 | 0.051 | 0.0510 | 0.051 |
| L-026 | 0.060 | 0.022 | 0.0600 | 0.0600 | 0.0600 | 0.060 | 0.0600 | 0.060 |
Summary of comparison of target value and assigned value are presented in table 6.

Table 6. Comparison of target value and assigned value.

| Parameter | Target Value (mg/L) | Assigned Value using Consensus from Expert Laboratory (mg/L) | Assigned Value using result from references value (mg/L) |
|-----------|---------------------|-----------------------------------------------------------|------------------------------------------------------|
| Fe        | 0.40                | 0.41                                                      | 0.40                                                 |
| Mn        | 0.30                | 0.31                                                      | 0.30                                                 |
| Cd        | 0.06                | 0.06                                                      | 0.06                                                 |
| Zn        | 0.08                | 0.08                                                      | 0.07                                                 |

The sample for laboratory proficiency testing of heavy metals in water should be prepared precisely, accurately and meet the requirements of ISO/IEC 17043:2010 [19]. This research indicated that the target values of Fe, Mn and Cd produced the same value as the assigned value obtained from consensus of expert laboratories and the reference value method. On the other hand, the result of reference value method differs from target value in the case of Zn. This may happen due to the broad variation of Zn data resulted from the participating laboratories [20].

Assigned values resulted from the expert laboratories consensus and reference value for Fe, Mn and Cd parameters were the same. This come out from several factors, such as laboratory personnel who conducted proficiency test were competence, proven by the results of intra-laboratory correlation or analyst proficiency tests; the testing method used has been validated or verified accordingly so that they meet the requirements and meet the stated objectives [21]. Calibration of volumetric glassware
used for the dilution of the proficiency test material traced to the international unit system meeting the acceptable limits, namely the amount of uncertainty and correction less than the tolerance of glassware also contributed in this case. AAS instrumentation used for testing proficiency test material have been tested on its performance to meet wavelength accuracy and absorbance sensitivity requirements. Environmental conditions such as temperature, humidity and dust particles were monitored to meet the requirements. All laboratories included in metrology road map have already accredited with ISO 17025, also they have experienced in testing environmental samples for more than 10 years [8].

The result of assigned values for Zn parameter using consensus of expert laboratories method is rather different to the assigned value of reference value. This phenomenon was probably due to Zn element nature, which is highly contained in dust particle, slight change of room condition including dust particles, temperature, and humidity of the room could be very influential.

4. Conclusion
Determination of assigned value through expert laboratories consensus method has obtained the similar value as target value set by P3KLL as proficiency test provider. However, since the method depends on the competency of the laboratories, it is important to review the competency of the expert laboratories on a regular basis to ensure the validity of the values produced.

5. Reference
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