

ESTIMATE OF UNCERTAINTY OF MEASUREMENT IN THE DETERMINATION OF Cu, Zn, Fe IN PROFICIENCY TEST (PT) DRINKING WATER SAMPLE

Kyauk Khe Sein¹, Ye Chan²

Abstract

Nowadays, the testing and calibration laboratories have to provide high confidence and globally acceptable of measurement results in order to support the important action or decision based on it, especially for international trade and customer satisfaction. Therefore, according to guide ISO/IEC 17025, the measurements should be carried out by using validated method of analysis, defining the internal quality control procedures, participating in proficiency testing schemes and establishing the traceability and uncertainty of the measurement results. For this reason the determination of metals in drinking water requires the use of validated methods which demonstrating their robustness and reliability. In this context the estimate of uncertainty is an important tool allowing the identification the influence of each step of the analytical protocol in the overall quality of the results. In this paper, it was discussed the estimate of uncertainty during the measurement of metals (Cu, Zn and Fe) in proficiency test (PT) drinking water sample by atomic absorption spectrometry in flame mode. The concentration of Cu, Zn, Fe found in PT drinking water is 1.601 ± 0.043 mg/L, 1.061 ± 0.202 mg/L and 0.179 ± 0.095 mg/L respectively. The total uncertainty for Cu, Zn and Fe were 3%, 19%, 53% respectively.

Keywords: uncertainty, AAS, proficiency test, ISO/IEC 17025

Introduction

Nowadays, the testing and calibration laboratories have to provide high confidence and globally acceptable of measurement results in order to support the important action or decision based on it, especially for international trade and customer satisfaction. Therefore, according to guide ISO/IEC 17025, the measurements should be carried out by using validated method of analysis, defining the internal quality control procedures, participating in proficiency testing schemes and establishing the traceability and uncertainty of the measurement results. The importance for uniform

¹. Assistant Lecturer, Universities' Research Centre, University of Yangon

². Professor, Head of Universities' Research Centre, University of Yangon

approach of measurement in estimation of uncertainty and its reporting has attracted metrologist globally. An evaluation, or at least full consideration, of all identifiable components that contribute to the uncertainty of a test result will allow valid results to be obtained and indicate the aspects of the test that require attention to improve procedures. In addition, systematic assessment of the factors influencing the results and its uncertainty forms a key of validation method.

According to EURACHEM/CITAC, the uncertainty can be defined as ‘a parameter associated with the result of measurement, which characterizes the dispersion of the values that could reasonably be attributed to the measurand’. In the other word, the estimation of uncertainty is a result of the various components which affects to the measurement. The evaluation of uncertainty requires the analyst to look closely at all the possible sources of uncertainty. Many possible sources of uncertainty may be arisen in practice such as sampling, sample effects (matrix effects and interferences), instrument effects, storage conditions, reagent purity, assumed stoichiometry, measurement condition, uncertainties of masses and volumetric equipment, reference values, computational effect, blank correction, operator effect, and random effect. In estimating the overall uncertainty, it may be necessary to take each source of uncertainty and treat it separately to obtain the contribution from that source. Each of the separate contributions of uncertainty is referred to as an uncertainty component, and known as standard uncertainty if it is expressed as a standard deviation. For a measurement result, the total uncertainty, termed combined standard uncertainty is calculated and obtained by combining all the uncertainty components. Furthermore, an expanded uncertainty should be used for most purposes in analytical chemistry. The expanded uncertainty provides an interval within which the value of measurand is believed to lie with a higher level confidence.

A good estimation of uncertainty can be made by concentrating effort to the largest contribution of source of uncertainty because the value obtained for the combined uncertainty is almost entirely controlled by the major contribution. Further, once uncertainty value evaluated for a given method applied in particular laboratory (i.e. particular measurement procedure), the uncertainty estimation obtained may be reliably apply to subsequent results

obtained by the method in the same laboratory, provided that this is justified by the relevant quality control data. No further effort should be necessary unless the procedure itself or the equipment used is changed, in which case the uncertainty estimation would be reviewed as part of the normal revalidation. In the other hand, the observed differences in result may be accounted for by the uncertainty associated with the result rather than real difference in properties or performance. Thus if two competent laboratory examine different sub samples from the same sample source by the same method and obtain numerically different results, these results may not be different when uncertainty of measurement is taken into account (Harry Budiman, et.al., 2009).

This paper describes the evaluation of uncertainty of measurement in determination of Cu, Zn, Fe content in drinking water PT sample using flame atomic absorption spectrometry. The specification of measurand, source of uncertainty, standard uncertainty, combined uncertainty and expanded uncertainty from this measurement were evaluated and accounted. The purpose of the evaluation of uncertainty in this measurement is to provide the bias taken place which depended on the various components or measurands that effect to the measurement. This is required for the laboratory participating in the Proficiency Testing Scheme: Analysis of drinking water and waste water by Universities' Research Centre, University of Yangon. The estimation of uncertainty measurement of each laboratory is needed by proficiency testing provider for comparison with the standard deviation for proficiency assesment (σP) that represents fitness-for-purposes over a whole application sector in proficiency testing scheme.

The objective of a measurement is to assign a magnitude to the measurand, the quantity intended to be measured. The assigned magnitude is considered to be the best estimate of the values of the measured. For a given result there is not one value, but an infinite number of values dispersed about the result within an interval. Hence measurement of a parameter is meaningless unless the width of interval within which the reported value of the measured is expected to disperse is specified. Material used for army purpose is to be tested in proper way because the chemical composition of material is most affecting factor in performance of final product. While testing

chemical composition the final result get affect by various factors so the composition result may not be so correct.

Experimental Section

2.1 Atomic Absorption Spectrophotometer

Atomic Absorption (AA) occurs when a ground state atom absorbs energy in the form of light of a specific wavelength and is elevated to an excited state. The amount of light energy absorbed at this wavelength will increase as the number of atoms of the selected element in the light path increases. The relationship between the amount of light absorbed and the concentration of analytes present in known standards can be used to determine unknown sample concentrations by measuring the amount of light they absorb. Simplified diagram of principle of AAS is shown in Fig. 1.

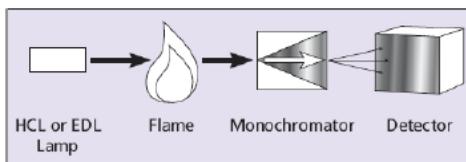


Figure 1: Simplified diagram of principle of AAS

The liquid sample is reduced to a vapor mist of atomic population by a nebulizer with support gas. Mixed with proper fuel, it is sprayed over the flame. The reference beam going around the flame is not affected because the energy of sample beam going through the flame is absorbed by the sample element present in the liquid sample and amount of absorption being proportional to the element concentration. Both these beam are combined together before entering the monochromatic region which selects the appropriate resonance line and direct it to the wide range photo multiplier tube. The electronics there after separates reference and sample signal in time reference single is used to compensate for drift in lamp intensities and sample signal is processed for photometric computation of the result. The atomic absorption Spectrophotometer (Perkin Elmer 900H) is as shown in Fig. 2.

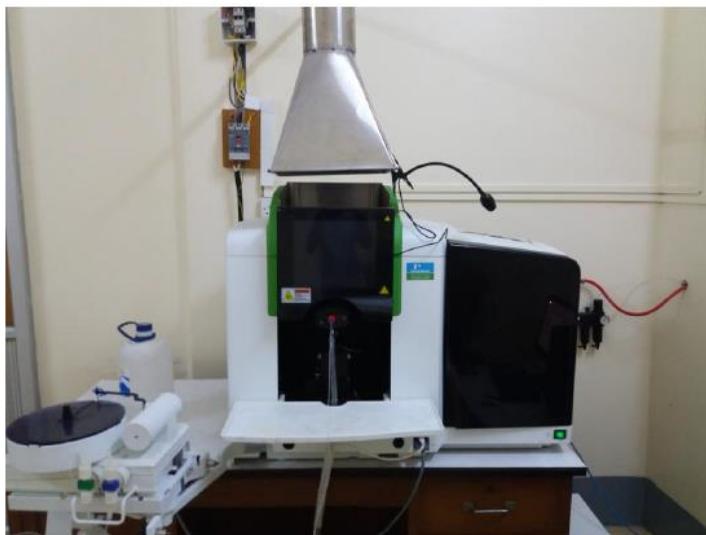


Figure 2: Atomic Absorption Spectrophotometer AAS (Perkin Elmer 900H)

2.2 Material

All chemicals were purchased from SIGMA-ALDRICH as shown in Fig. 3 and for analysis grade. Pure deionized water was used for all solution preparation. Calibration of standard Cu, Zn, Fe solution was prepared by the dilution of titrisol of Cu, Zn, Fe solution 1000 ± 4 mg/L as stock solution. The test sample is clean water for drink which prepared and distributed by LIPI Indonesia as shown in Fig. 4.



Figure 3: Cu and Zn Standard for calibration



Figure 4: Proficiency test (PT) sample

2.3 Principle of working

When a liquid sample containing a chemical constituent element of interest is reduced to a spray mist of atomic vapour, mixed with proper fuel and burn over a burner head and if light radiation of the same element from a emitting source is passed through the flame, as atoms of the element in the sample vapour are present in ground state of unexcited condition they absorb amount of corresponding radiation passing through the flame. Amount of absorption by the analyst depend on its concentration in the sample and are directly proportional to each other. Hence measurement of absorption value forms the base for calculation of its concentration in sample (EURACHEM/ CITA Guide CG4, 2012).

2.4 Method of Analysis

Every time when an element is estimated, the system is calibrated by aspirating a set of different strength standard solution of known concentration of the element and graphical representation of absorbance verses concentration is made to get a liner graph for the standard solution. When an unknown sample is aspirated in the same condition, with reference to its measured absorbance and the standard graph concentration of the element in test sample is displayed in part per million (ppm) or mg/L.

Result and Discussion

3.1 Identification of sources of uncertainty

The sources of uncertainty for the method were identified by constructing a cause-and-effect (fish bone) diagram Fig.5 widely cited by some authors EURACHEM/CITAC Guide CG 4.

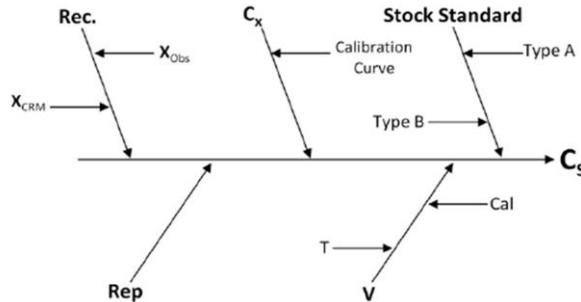


Figure 5: Sources of uncertainty fish bone diagram

3.1.1 Concentration of aliquot sample, C_x

As shown in Fig. 5 the uncertainty associated with the concentration of the Cu, Zn, Fe in the sample aliquot is estimated from calibration curve. The uncertainty of aliquot sample analyzed, represented by $\mu(C_x)$, is given by EURACHEM/ CITA Guide CG4. And equation (1) and (2) is used to calculate the uncertainty of aliquot sample.

$$S_{y/x} = \sqrt{\frac{\sum(Y_i - Y_c)^2}{(n-2)}} \tag{1}$$

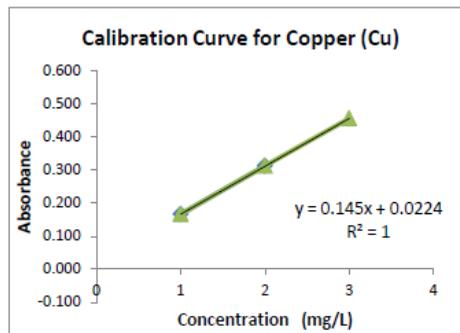
$$\mu(C_x) = \frac{S_{y/x}}{b} \sqrt{\frac{1}{m} + \frac{1}{n} + \frac{(Y_{spl} - Y_{mean})^2}{b^2 \cdot \sum(X_i - X_{mean})^2}} \tag{2}$$

Where, b = slope of the calibration curve,

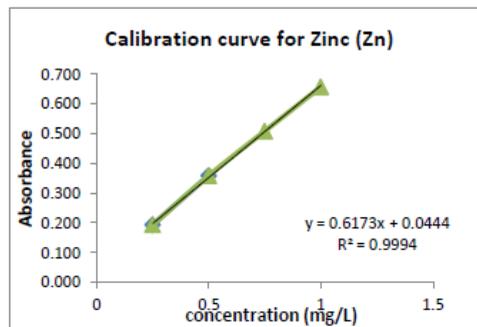
m = number of measurements to determine C_o,

n = number of measurements for the calibration,

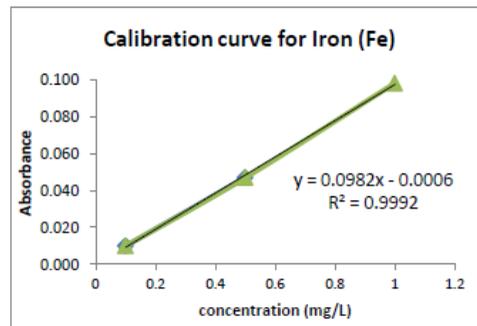
S_{y/x} = residual standard deviation.



(i)



(ii)



(iii)

Figure 6: Standard calibration curve graph for (i) Copper (Cu) (ii) Zinc (Zn) (iii) Iron (Fe)

3.1.2 Recovery (Rec.)

The uncertainty from recovery is calculated by using equation (3) as percentage recovery from comparable reference material. The recovery, R, has an uncertainty associated with the certified reference material value used and with the variability of the particular measurement of the solution analyzed.

$$\mu(\text{Rec}) = \text{Rec} \cdot \sqrt{\left(\frac{\mu(X_{\text{Obs}})}{X_{\text{Obs}}}\right)^2 + \left(\frac{\mu(X_{\text{CRM}})}{X_{\text{CRM}}}\right)^2} \tag{3}$$

3.1.3 Repeatability (Rep)

Fig.5 shows two major contributions to the uncertainty associated with the repeatability, instrument drift and precision associated with the dilution of calibration solutions.

3.1.4 Stock Standard (C_{0.5})

The uncertainty from stock standard is calculated by using equation (4).

$$C_{0.5} = C_{1000} \times \frac{V_1}{V_{100}} \tag{4}$$

Table 1: Calculated standard uncertainty arising from uncertainty sources

	Standard uncertainty arising from C _x (mg/L)	Uncertainty arising from Repeatability (Rep)	Uncertainty arising from Recovery (Rec.) (%)	Uncertainty arising from Stock Standard		Combined uncertainty C _s (mg/L)
				Type A (mg/L)	Type B (mg/L)	
Cu	0.0032	0.0049	1.1682	0.0005	4	0.022
Zn	0.0989	0.0113	1.3330	0.0005	4	0.101
Fe	0.0472	0.0278	1.1680	0.0005	4	0.048

3.2 Combined Standard Uncertainty

The value of parameters for calculation of Cu, Zn, Fe concentration in sample, equation (1), their standard uncertainties and their relative standard uncertainties were summarized in Table 1. According to the data of combined

uncertainty, it is found that Fe is more error percent than Cu and Zn elements and Cu is least error.

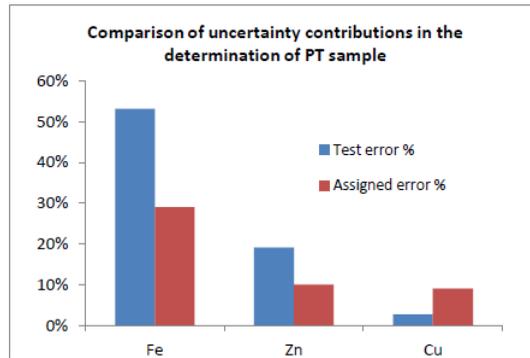


Figure 7: Comparison of error in PT sample

Fig. 7 shows the comparison of error percentage of estimate assigned error and estimate the test error in PT sample. It is found that the error of Fe element is greater than other elements but Cu is smaller for our calculation because relative standard deviation of Fe is greater than Cu in the calibration curved. This is due to chemical interference on atomization process.

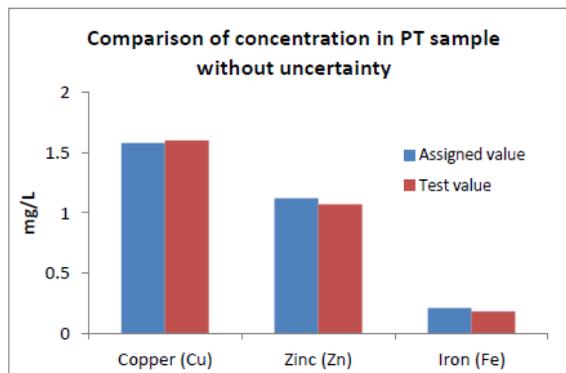


Figure 8: Comparison of concentration in PT sample with assigned value and test value without using uncertainty

Fig. 8 shows the comparison of concentration in PT sample with assigned value and test value without using uncertainty. It is found that the concentrations of elements of our test value are nearly equal to the assigned value of PT coordinator.

Table 2: Comparison of assigned value of PT coordinator and our test value with uncertainty

Measurands	Assigned value with uncertainty (mg/L)	Test value with uncertainty (mg/L)
Copper (Cu)	1.58 ± 0.14	1.601 ± 0.043
Zinc (Zn)	1.12 ± 0.11	1.065 ± 0.202
Iron (Fe)	0.21 ± 0.06	0.178 ± 0.095

It is found that the concentration results of the determination of Cu, Zn, Fe in PT sample are reliable with assigned value when measurement uncertainty is added as shown in Table 2.

Conclusion

The Cu, Zn, Fe content in drinking water PT sample analyzed by Flame AAS was 1.601 ± 0.043 mg/L, 1.065 ± 0.202 mg/L, 0.178 ± 0.095 mg/L at 95% confidence level. The total uncertainty for Cu, Zn and Fe were 3%, 19%, 53% respectively. The sources of uncertainty in the determination of Cu, Zn, Fe in sample by AAS were the uncertainties of concentration of Cu, Zn, Fe obtained by AAS, the uncertainties of mass of sample, the uncertainties of dilution factor, the uncertainties of the volume of sample, the uncertainties of repeatability and the uncertainties of recovery. The uncertainty estimation of different sources in analysis Cu, Zn and Fe demonstrated that the calibration curve was the major contribution to the uncertainty of the final results. Even if the result of the measurement is not perfect, it is possible to obtain reliable information, since the result of the measurement is associated with its respective uncertainty. The success in estimating uncertainty of measurement depends on correct analysis of the whole measuring process. Estimation of measurement uncertainty is very important for reliability of measurement data. This paper shows the effects of individual factors and its importance on final result. Evaluation of uncertainty gives idea about various factors affecting the test results. Accordingly proper actions can take to reduce the effect of factor which is affecting more. This helps to improve the quality of testing and calibration method. In case of AAS repeatability is affecting more, so while performing the test standard procedure should be followed which help to minimize the uncertainty of measurement.

References

- Ellison, S.L.R., Rosslein, M., and Williams, A., *EURACHEM/CITAC Guide CG 4*, (2012), "*Quantifying Uncertainty in Analytical Measurement*", Third Edition.
- Harry Budiman*, Fransiska Sri H. Krismastuti, and Nuryatini, (2009), "*Estimation of Measurement Uncertainty in the Determination of Fe Content in Powdered Tonic Food Drink Using Graphite Furnace Atomic*", Research Centre for Chemistry, Indonesian Institute of Sciences, Kawasan PUSPIPTEK Serpong, Banten 15314, Indonesia.
- Kirkup, L., (2007), "*Calculating and Expressing Uncertainty in Measurement*", University of Technology, Sydney.
- Neha S. Mahajan et al., (2012), "*Analysis of Uncertainty Measurement In Atomic Absorption Spectrophotometer*", International Journal of Engineering Science and Technology (IJEST), ISSN : 0975-5462 Vol. 4.
- V. J. Barwick, S. L. R. Ellison, B. Fairman, (1999), "*Estimation of uncertainties in ICP-MS analysis: a practical methodology*", *Analytica Chimica Acta* 394, pp. 281-291.