An interlaboratory comparison of INAA analytical method for coal fly ash elemental characterization

Endah Damastuti, Muhayatun Santoso, Saiful Yusuf, and Woro Yatu N.S.

Center for Applied Nuclear Science and Technology – National Nuclear Energy Agency, Jl. Tamansari 71, Bandung, Indonesia
Center for Advanced Material Science and Technology – National Nuclear Energy Agency, Kawasan Puspiptek Serpong, Indonesia
e-mail: endah_dt@batan.go.id

Abstract. Quality assurance of analytical results has become the high market demand in this globalization era. Accurate and reliable for analytical data is one of the requirements for a testing laboratory to get recognition from customers and institutions that issue certificates, which may be obtained by ensuring the validity of the used analytical methods. Validation of methods applied by laboratories can be done; one of by conducting proficiency tests or inter-laboratory comparative tests. We have been conducted the Inter-laboratory comparative tests for Neutron Activation Analysis for elemental characterization of coal fly ash. Coal fly ash samples were prepared according to ISO Guide 34 and 35, and distributed to eleven NAA laboratories in Indonesia as well as in other countries. As much as 18 elements should be analyzed by participant laboratories. The results were processed statistically using Z-score where it found that three elements (Hg, Se, and Mg) cannot be evaluated due to insufficient data and also high variations of the data, while for other elements such as As, Th, Na, and Sb showed a good agreement among participant laboratories. Through this inter-laboratory comparative testing program, it is expected that NAA laboratories, especially in BATAN, can maintain and improve their performance and quality of their analytical results.

1. Introduction
National energy consumption increases along with economic and population growth. To fulfill the need of energy, the Indonesian government has launched various programs related to this matter, one of is the fast track program 20000 MW since 2006 which comprises many coal-fired power plants development mainly in Java and Bali. The coal combustion from coal-fired power plants in Indonesia produces combustion by-products in the form of gases and solid materials. Coal fly ash is one of coal combustion by-products that has fine particles which contributes to the enhancement of PM, concentration in the air and the toxic elements in it as well. Coal fly ash has an adverse effect on the environment and also as a significant source of the potentially toxic element [1], [2]. Due to its effect to the environment and human health indirectly, many researchers all over the world are getting interested into fly ash focuses on the measurement of trace element concentration, the leaching of the elements into the environment and also the behavior of the elements generated by coal combustion [3], [4], [5]. Subsequent evaluation associated with environmental and biological risks usually begins with the determination of minor and major elements qualitatively and quantitatively. Regarding that many crucial policies or decisions related to public or individual health, environmental protection and international trade are based on the results of analytical measurement hence the reliability of analytical
result has to be assured, which can be achieved one of through ensuring the validity and reliability of the analytical method [6]. Validating of the analytical method used by the laboratory may be accomplished one of through participating in proficiency or interlaboratory comparison testing as required in ISO/IEC 17025.

Neutron Activation Analysis (NAA) is an advanced analytical method for the determination of elements which is based upon the conversion of stable nuclei to other, mostly radioactive nuclei, through fission nuclear reaction and measurement of irradiation emitted by reaction products [7]. NAA is a nuclear analytical technique that is very accurate and sensitive, non-destructive, does not require complicated sample preparation and can measure many elements and rare earth metals with good accuracy [8]. NAA is also acknowledged as a primary method of measurement especially for reference material certification [7], [8], [9]. Since NAA is analytical techniques that utilized nuclear science and technology, BATAN has responsibility for mastering and its application in various fields. There are several NAA laboratories in BATAN that should be assured of their performance. Interlaboratory comparison is one of the methods used for regularly assessing the accuracy of the analytical data produced by laboratories for particular measurements [10], [11]. We conducted an interlaboratory comparison with objectives to ensure that data generated within the NAA laboratories are comparable and have high quality hence will enhance the performance of the NAA laboratory in elemental characterization especially in environmental samples. The interlaboratory comparison was carried out for determining elemental content in coal fly ash by means of INAA. The coal fly ash samples used in this interlaboratory comparison is developed as a new candidate of reference material. Therefore, this interlaboratory comparison is also as a scheme program of a subsequent step toward its certification.

2. Methodology

Participating laboratories

As much as 2 g of coal fly ash samples in 50mL of polyethylene bottle was distributed to eleven NAA laboratories. The eleven NAA laboratories participated in the study comprises seven participants from Indonesia, and three participants from NAA laboratories in Australia, Korea, and China, with one contributing with two different NAA methods, giving a total of eleven participants, later denoted as Laboratory 1–11.

Preparation of coal fly ash sample

The coal fly ash used for this interlaboratory comparison study is a new candidate for reference materials, therefore, it was prepared according to ISO Guide 34 and 35. The samples of coal fly ash in this work were obtained from the coal-fired power plant in Central Java, Indonesia. As much as 10 kg of coal fly ash was collected from the electrostatic precipitator and were used to produce the reference material candidate. The bulk material was dried in the closed cabinet, heated by an infrared lamp with temperature set not more than 50ºC for 3 days. The dried coal fly ash was grinded using mortar agate and sieved with 75 µm sieve (200 mesh). Afterward, the coal fly ash was homogenized by manually mixing and repetitive quartering-coning, before being divided and placed in a series of bulk containers (Nalgene HDPE bottle, 1000 mL). The coal fly ash was tested for its homogeneity and then distribute representatively into a 60 mL capacity of high-density polyethylene bottles. Approximately 50 g of the material was transferred to each bottle. A total of more than 150 bottles were then labelled with the name of the material and serial number. The bottles were kept in dry cabinet storage. For interlaboratory comparison purposes, 10 bottles were randomly selected and 2 g portion was taken into polyethylene bottle to sent to participant laboratories.

Measurement and collection of the results

All laboratories were assured anonymity and accordingly their results are presented without any designation. Laboratories were responsible for their own sample handling, and data reporting.
Participating laboratories were assigned to analyze Aluminium (Al), Arsenic (As), Barium (Ba), Calcium (Ca), Chrome (Cr), Iron (Fe), Mercury (Hg), Potassium (K), Magnesium (Mg), Manganese (Mn), Sodium (Na), Antimony (Sb), Selenium (Se), Strontium (Sr), Thorium (Th), Titanium (Ti), Uranium (U) and Vanadium (V) using INAA method. The participant laboratories were allowed to conduct their analysis whether by comparative NAA method or k₀-NAA method. The value of each parameter was requested to be reported in the report form where the unit of expression and number of significant decimal places were indicated and along with their uncertainty values (expanded uncertainty with a coverage factor = 2). Several laboratories did not perform measurements of all parameters. Thus, the total number of results reported for each parameter differs. Participants were asked to provide final, calibrated, measurement results for each of the parameters they determined, noting whenever more than one analysis for a particular parameter was done out of a single bottle. Additionally, laboratories were asked to indicate how the measurements were made (including equipment); how the measurement data were calibrated and an assessment of the uncertainty; and finally, if any adjustment was made to the data prior to reporting.

**Statistical Evaluation**

The homogeneity of the test materials is a fundamental requirement for all inter-laboratory studies. For homogeneity testing as much as 12 bottles were randomly selected and analyzed in duplicate under repeatability conditions. Homogeneity testing was carried out using NAA methods. The overall sample homogeneity was assessed by a One-way analysis of variance (ANOVA) without removing any values [12]. The samples were considered homogeneous if the F-test values were smaller than those of the critical values at 95% confidence interval.

Identification of probable outlier results was performed using Grubbs’ test to identify deviating mean values (reported by the participants)[13]. Grubbs provides different outlier tests, for single outliers (highest or lowest value), and for double outliers (two highest or two lowest values)[11]. For single outlier (highest or lowest value) was evaluated using equation (1) while for double outliers were evaluated by equation (2):

\[ G_{1(highest/lowest)} = \frac{|\bar{x} - x_i|}{s} \]  
\[ G_{3(highest pair/highest pair)} = 1 - \left[ \frac{(n-3)s_{n-2}^2}{(n-1)s^2} \right] \]  

Where \( s \) is standard deviation of all results, \( \bar{x} \) is the average value of all results, \( x_i \) is evaluated value, and \( s_{n-2} \) is a standard deviation of all results without two highest or two lowest values.

Assessment of the laboratory performance was carried out by evaluating the variation of all data results using z-score. Z-score was the most widespread methods to evaluate the laboratory bias [12], [14]. A z-score is the ratio of the bias estimate and the target value for the standard deviation of the results [11] as described by the following equation:

\[ Z-score = \frac{x_i - X}{s} \]
of the z-scores, which are standardized, allow direct estimation of the performance of the laboratory by comparison with the following quality limits:
- $Z < 2$: the performance of the laboratory is considered satisfactory.
- $2 < Z < 3$: the performance of the laboratory is considered questionable.
- $Z > 3$: the performance of the laboratory is considered unsatisfactory.

3. Results and Discussion
Sample homogeneity was evaluated using the duplicate results of representative elements derived from 12 bottles. The representative elements are Arsenic (As), Calcium (Ca), Manganese (Mn) and Uranium (U). These elements were chosen as representatives based on the amount of elemental concentration in the coal fly ash samples i.e. major, minor and trace levels. A summary of homogeneity test results is shown in Table 1. As can be seen from Table 1, the F-values from ANOVA for all components in the prepared test materials were lower than the critical F-value. The results indicated that the sub-samples were considered sufficiently homogeneous to be used as test materials for laboratory performance study.

| Element          | Mean result (mg/kg) | F-value | F-critical (p=0.05) | Results   |
|------------------|---------------------|---------|---------------------|-----------|
| Arsenic (As)     | 16.13               | 2.080   | 2.717               | Homogeneous |
| Calcium (Ca)     | 39.367              | 1.892   | 2.717               | Homogeneous |
| Manganese (Mn)   | 921.65              | 1.471   | 2.717               | Homogeneous |
| Uranium (U)      | 7.72                | 2.151   | 2.717               | Homogeneous |

$^1$F-value < Critical F-value, sample is homogeneous

| Table 2. Resume of the number of data reported and evaluated by outlier Grubbs’ test |
|----------------------------------------|--------|--------|--------|--------|--------|--------|--------|
| Number of laboratories                 | Al     | As     | Ba     | Ca     | Cr     | Fe     | K      | Mn     | Na     | Sb     | Sr     | Th     | Ti     | U      | V      |
| Reported results                       | 8      | 11     | 9      | 8      | 11     | 11     | 9      | 8      | 11     | 9      | 7      | 11     | 8      | 8      | 8      |
| Not reported                           | 3      | 0      | 2      | 3      | 0      | 2      | 3      | 0      | 2      | 4      | 0      | 3      | 3      | 3      | 3      |
| Outlier                                | 1      | 1      | 0      | 1      | 2      | 1      | 2      | 1      | 2      | 1      | 0      | 1      | 1      | 0      | 1      |
| Data evaluated by Z-Score              | 7      | 10     | 9      | 7      | 10     | 9      | 7      | 7      | 9      | 8      | 7      | 10     | 7      | 8      | 7      |

To the eleven participant laboratories, 18 elements (Al, As, Ba, Ca, Cr, Fe, Hg, K, Mg, Mn, Na, Sb, Se, Sr, Th, Ti, U, and V) were required to be measured by NAA analytical methods. The reported results yield only 15 elements that statistically sufficient and able to further calculation. The other three elements that cannot be further evaluated were Hg, Se, and Mg. In mercury determination, only one of 11 laboratories who has reported their Hg value, while for Selenium, only four laboratories reported their selenium values. Thus, the data results of mercury and selenium were statistically insufficient. On the contrary, for magnesium determination as many as 8 laboratories have reported their results which are sufficient statistically unfortunately, the variation is too large. The standard deviation of all results of Mg was found as much as 46.8% and it also cannot be evaluated using Grubbs’ test therefore, these data cannot be further analysed to z-score calculation. Several laboratories did not perform measurements of all parameters. Thus, the total number of results reported for each parameter differs. The Z-score was calculated after Grubbs’ test was performed. Table 2 showed the resume of the total number of data reported and evaluated the results of The Grubbs’ outlier test. The data evaluated for Z-score are around 78 – 100% of all reported data. Almost all elements have outlier data except for Ba, Sr, and U.
Participant laboratories were requested to perform measurements of required elements using NAA analytical method with their own analytical protocols for the measurement of the concentrations of elements currently being determined in their laboratory such as the amount of samples used to analysis, the standards used, the optimum irradiation and counting time, the performed of spectrum and data analysis, etc. The analytical performance of each laboratory was evaluated based on z-score between laboratory variation calculation and identified as satisfactory, questionable and unsatisfactory results. A summary of the results of the z-score values for each parameter tested is presented in Figure 1.
I-Concern19

Figure 1. Z-score values of each laboratory for determination of (a) Al, (b) As, (c) Ba, (d) Ca, (e) Cr, (f) Fe, (g) K, (h) Mn, (i) Na, (j) Sb, (k) Sr, (l) Th, (m) Ti, (n) U and (o) V in coal fly ash samples.

The discussion related to the Z-score results will be divided into three parts based on the amount of element concentrations in coal fly ash samples i.e. Major elements, Minor elements, and Trace elements. Major elements in coal fly ash are Al, Ca, Fe, K, Na, and Ti. Minor elements are Mn, Ba, Sr, Cr, and V, while trace elements are As, Sb, Th, and U. Figure 1 showed that for some of major elements, the z-score values were varied and most of them were unsatisfactory. Aluminium, Calcium, and Titanium have the most unsatisfactory results among others. The z-scores of the submitted aluminium values based on median value and target SD Horwitz showed that 2 values out of 8 or 25% of submitted data were identified as satisfactory results, while other 12.5% and 62.5% were found as questionable and unsatisfactory results respectively. For calcium, 3 laboratories out of 8 or 37.5% were identified as good performance laboratories with satisfactory results, while other laboratories or 62.5% got unsatisfactory results. And for titanium gave 37.5% or 3 out of 8 submitted data were satisfactory results, 12.5% were questionable results and 50% were unsatisfactory. The other major elements tested such as Fe, K and Na gave more than 50% of the submitted data found as satisfactory results, and their concentration in coal fly ash is high or found in % amount. Aluminium concentration in coal fly ash range of 10-11%, the highest among other elements. It has very short of half-lived and is easily activated by thermal neutron. This condition often gives problems due to its high activity rate, and for safety reason sometimes, the samples are not allowed to further analyzed by gamma spectrometer and should be cooled first, which may lead to non-optimal measurement. Furthermore, for major elements determination in comparative NAA method, the optimum of the amount of the standard used should be considered properly as well as optimum irradiation and counting conditions.

Based on the z-scores for minor elements; Cr and Sr, gave only about of 18.2% and 28.6% of submitted data were satisfactory. Most of z-score results for chromium and strontium were found questionable, 45.5% and 42.9% respectively. While for Ba, Mn, and V, the z-score calculation yields that more than 50% of laboratories have satisfactory results; 66.7%, 75% and 75% respectively. The satisfactory results also obtained for all tested trace elements. The z-score calculation for trace elements resulted that more than 70% of laboratories have a satisfactory result. For antimony and uranium gave 77.8% and 75% of satisfactory results respectively, while for As and Th gave more satisfying results with 90.9% or 10 out of 11 participated laboratories have z-score in a satisfactory area. The used of classical Horwitz equation for targeted standard deviation in z-score calculation gives a narrow range of acceptable areas for major element concentrations in the sample. This could be one of the reasons that most of the results of major elements were unsatisfactory. Horwitz equation is a functional relationship between the reproducibility precision and the concentration of the analyte examined based on more than 7500 method performance studies (11). For each decrease of concentration by a factor of 100, the reproducibility is doubled, thus for trace level of analyte concentration will have a wider acceptable area of z-score. However, the Horwitz standard deviation is
as one of the precision criteria widely used for method performance testing and in general, gives better consideration on method performance evaluation. Based on these interlaboratory comparison results, the performance of each laboratory is known. Laboratory 11 is the a good performance laboratory that has passed 100% or 9 out of 9 submitted data and has satisfactory results. The majority of the participant laboratories have passed more than 50% of their results to be satisfactory, while there are three laboratories that only have less than 50% of their submitted data were accepted. These results showed that the among of participated laboratories were not have equal performance in applying NAA analytical method for elemental determination in coal fly ash yet. Some improvements should be made. For those laboratories who have questionable or unsatisfactory or outlier results should investigate the root of the problems existed and identified the analytical steps that have probability gives a high error. The harmonization of analytical protocols of the NAA method for elemental concentration in coal fly ash samples should be carried out to enhance the NAA laboratory capabilities.

The improvements also should be made for interlaboratory comparison conducted. The assigned value used on this interlaboratory comparison is based on consensus value. Even the used of consensus value has the advantages include low cost, it does not need requires additional analytical work, the calculation of the value is usually straightforward and the acceptance among participants is often good, the consensus value still has disadvantages that it is not independent to the participants results and may have higher uncertainty when the number of laboratories is small (14). The used of the consensus value may hiding the potential bias of the population as the assigned value will follow the population. For the small number of laboratories included in an interlaboratory comparison the assigned value from reference laboratories or reference materials is the best option in evaluation laboratory performance especially on the using of a same analytical method.

4. Conclusions
We have conducted an interlaboratory comparison for the elemental determination in coal fly ash sample using Neutron Activation Analysis analytical method. As many as 18 elements were required to be measured. It was found that 3 out of 18 elements namely Hg, Se and Mg, were not able to further analyzed due to the lack and the large variations of the data reported. Although the analytical results for certain elements differed among the laboratories, the results showed that for the elemental concentration in a minor and trace levels from most of participating laboratories were in a good agreement. While for the major elements need further improvement especially for the elements having short half-live and high concentrations level in the samples. The overall, it was found that the performance among the laboratories applying NAA method for elemental determination in coal fly ash sample was not equal yet that may lead to the conclusion that harmonization of analytical protocols should be carried out especially in order to support the enhancement of the NAA laboratories capability in BATAN.

Acknowledgment
The authors would like to acknowledge the National Nuclear Energy Agency (BATAN) Indonesia for the financial support and the Indonesia NAA Forum (FAANI) for providing this interlaboratory comparison. We would also like to acknowledge the colleagues in The Center for Applied Nuclear Science and Technology, Bandung; and Center for Advanced Material of Science and Technology, Serpong, for their assistance in preparing the tested material and data analysis.

References
[1]. Dai S, Zhao L, Peng S, Chou C, Wang X, Zhang Y, et al. International Journal of Coal Geology Abundances and distribution of minerals and elements in high-alumina coal fly ash from the Jungar Power Plant, Inner Mongolia, China. Int J Coal Geol [Internet]. 2010;81(4):320–32. Available from: http://dx.doi.org/10.1016/j.coal.2009.03.005
[2]. Marrero J, Polla G, Rebagliati RJ, Plá R, Gómez D, Smichowski P. Characterization and
determination of 28 elements in fly ashes collected in a thermal power plant in Argentina using different instrumental techniques. Spectrochim Acta Part B. 2007;62:101–8.

[3]. Al-arequi WM, Majid AA, Sarmani S. ANALYSIS OF TRACE ELEMENTS IN POWER PLANT AND INDUSTRIAL INCINERATOR FLY ASHES BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA). Malaysian J Anal Sci. 2008;12(2):375–9.

[4]. Goodarzi F, Sanei H. Plerosphere and its role in reduction of emitted fine fly ash particles from pulverized coal-fired power plants. Fuel [Internet]. 2009;88(2):382–6. Available from: http://dx.doi.org/10.1016/j.fuel.2008.08.015

[5]. Izquierdo M, Querol X. Leaching behaviour of elements from coal combustion fly ash: An overview. Int J Coal Geol [Internet]. 2012;94:54–66. Available from: http://dx.doi.org/10.1016/j.coal.2011.10.006

[6]. Sobiech-matura K. Radioactivity monitoring in foodstuff and drinking water - An overview of performance of EU laboratories based on interlaboratory comparisons t e. 2017;72.

[7]. Greenberg RR, Bode P, Nadai EA De, Bode P. Neutron activation analysis: A primary method of measurement Chapter 1. Neutron activation analysis: Principles and analytical characteristics. Spectrochim Acta Part B At Spectrosc [Internet]. 2011;66(3–4):193–241. Available from: http://dx.doi.org/10.1016/j.sab.2010.12.011

[8]. Á KP, Kang N, Cho K, Lee J. Determination of Cd and Cr in an ABS candidate reference material by instrumental neutron activation analysis. 2008;66:1913–5.

[9]. Park K, Min H, Yim Y, Yim Y, Hwang E, Cho K. Instrumental neutron activation analysis ( INAA ) and isotole dilution-inductively coupled plasma mass spectrometry ( ID-ICP / MS ) for certification of multielements in a tuna fish candidate certified reference material. J Food Compos Anal [Internet]. 2011;24(7):1064–8. Available from: http://dx.doi.org/10.1016/j.jfca.2011.01.009

[10]. Du JZ, Moore WS, Hsh HF, Wang GZ, Scholten J, Henderson P, et al. Inter-comparison of radium analysis in coastal sea water of the Asian region. Mar Chem. 2013;156:138–45.

[11]. Hund E, Massart DL, Smeyers-verbeke J. Inter-laboratory studies in analytical chemistry. 2000;423:145–65.

[12]. Puwastien P, Judprasong K, Pinprapai N. Development of rice reference material and its use for evaluation of analytical performance of food analysis laboratories. J Food Compos Anal. 2009;22:453–62.

[13]. Lundstedt S, Bandowe BAM, Wilcke W, Boll E, Christensen JH, Vila J, et al. First intercomparison study on the analysis of oxygenated polycyclic aromatic hydrocarbons (oxy-PAHs) and nitrogen heterocyclic polycyclic aromatic compounds (N-PACs) in contaminated soil. TrAC - Trends Anal Chem [Internet]. 2014;57:83–92. Available from: http://dx.doi.org/10.1016/j.trac.2014.01.007

[14]. Union I, Pure OF, Chemistry A, Division AC, Working I, For P, et al. THE INTERNATIONAL HARMONIZED PROTOCOL FOR THE PROFICIENCY TESTING OF ANALYTICAL CHEMISTRY LABORATORIES ( IUPAC Technical Report ) The International Harmonized Protocol for the proficiency testing of analytical ( IUPAC Technical Report ). 2006;78(1):145–96.

[15]. Bohm DA, Stachel CS, Hackenberg R, Gowik P. Preparation and characterisation of in-house reference material of tylosin in honey and results of a proficiency test. Anal Chim Acta [Internet]. 2011;700(1–2):58–62. Available from: http://dx.doi.org/10.1016/j.aca.2011.01.058