
ELEMENTAL CHARACTERIZATION OF COAL FLY ASH BY NEUTRON ACTIVATION ANALYSIS TOWARDS REFERENCE MATERIAL CERTIFICATION

Karakterisasi Unsur dalam Abu Terbang Batubara menggunakan Analisis Aktivasi Neutron Menuju Sertifikasi Bahan Acuan

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Abstract

Coal combustion by-products, such as coal fly ash, has known as a significant source of potentially toxic elements that may affect the environment since the increase of coal utilization as power fuel in Indonesia. Issuing the policies to protect the environment and public health is often based on analytical results. The quality of data analysis is very important since many crucial policies related to public health and environmental protections are based on the analytical results. Considering the need for reference material in ensuring the validity and reliability of the analytical results, reference material candidate of coal fly ash is being developed. Elemental characterization as one of the important parts in certifying the reference material is carried out using Neutron Activation Analysis (NAA) since it considered as high accuracy analytical method and commonly used to certified many reference materials throughout the world. Our NAA facility performance was assessed through optimizing analytical conditions by varying samples weight, method validation, and comparison test with other techniques as well. As much as 25, 100, and 250 mg of sample weight were assessed for its homogeneity effect. Method validation using SRM NIST 1633b had shown good results with bias not more than 10% compared to its certificate values. A comparison test with other results also showed a great agreement.

Kata kunci: coal fly ash, elemental characterization, NAA, reference material.

Abstrak

Produk sampingan pembakaran batubara, seperti abu terbang batubara, memiliki kontribusi terhadap unsur-unsur toksik yang berdampak terhadap kualitas lingkungan semenjak adanya peningkatan penggunaan batubara sebagai sumber energi di Indonesia. Dalam usaha perlindungan lingkungan dan kesehatan masyarakat, perlu dilakukan pengambilan kebijakan. Kebijakan yang dikeluarkan terkait hal tersebut kerap kali didasarkan pada suatu hasil analisis, sehingga suatu hasil analisis harus terjamin validitasnya dan dapat dipertanggungjawabkan, yang dapat tercapai melalui penggunaan bahan acuan. Oleh karena itu, dikembangkanlah bahan acuan dengan matriks abu terbang batubara. Karakterisasi unsur, salah satu tahapan penting dalam mensertifikasi bahan acuan, dilakukan menggunakan teknik Analisis Aktivasi Neutron (AAN) yang merupakan teknik analisis dengan tingkat akurasi tinggi dan umum digunakan dalam mensertifikasi bahan acuan di berbagai negara. Unjuk kinerja teknik AAN dilakukan melalui optimasi kondisi analisis dengan memvariasikan berat sampel, validasi metode dan uji banding dengan metode analisis lainnya. Sebanyak 25, 100 dan 250 mg sampel diuji sifat homogenitasnya. Validasi metode menggunakan SRM NIST 1633b menunjukkan hasil yang baik dengan bias kurang dari 10% dibandingkan dengan nilai sertifikat. Uji banding menggunakan teknik analisis lain, XRF, juga menunjukkan kesesuaian yang cukup baik.

Kata kunci: AAN, abu terbang batubara, bahan acuan, karakterisasi unsur.

1. INTRODUCTION

The increase of coal utilization as power fuel has gained many interests due to its adverse effect on the environment. The coal combustion by-products have known as a significant source of a potentially toxic element that affects the environment especially to the population in the

vicinity of the industrial area (Marrero *et al.*, 2007). Coal combustion by-products are known as sources of pollution that can give considerable impact on the environment whether in the form of gas and solids (Choudry, Nurgis, Sharif, Mahmood, & Abbasi, 2010; Marrero *et al.*, 2007; Wang, Dai, Zou, French, & Graham, 2019). Coal combustion exhaust gases such as

SO_x, NO_x, and CO₂, will be directly discharged into the air. Another coal combustion by-product is coal ash. Coal ash is composed of fly ash of 75-80% and bottom ash by 20-25%. (Bhatt *et al.*, 2019; Goodarzi, 2006; Rautray, Behera, Badapanda, Vijayan, & Panigrahi, 2009).

Coal fly ash has a fine particle size that some fraction of its release to the air and tends to travel due to the wind. Coal fly ash is contributing to enhancing the concentration of PM_{2.5} and the potentially toxic elements in it as well. Determination of minor and major elements qualitatively and quantitatively is usually the first step that must be taken towards a subsequent evaluation of the environmental and biological risks. Many research all over the world focuses into fly ash on the measurement of trace element concentration, the leaching of the element into the environment and also the behavior of the elements generated by coal combustion (Al-areqi, Majid, & Sarmani, 2008; Goodarzi & Sanei, 2009; Ibrahim, 2016; Izquierdo & Querol, 2012; Jones, McCarthy, & Booth, 2006; Masaki *et al.*, 2018). Moreover, the Indonesia government has established the 30MW of coal power plant crash program due to the fulfillment of electricity demand, especially on Java island.

As it can bring adverse effects to the environment and also human health, the characterization of coal fly ash needs to be done. However, to ensure the reliability, accuracy, and precision of the measurement, using appropriate certified reference materials (CRMs) is the best approach (Durbiano *et al.*, 2011; Wysocka & Vassileva, 2016). This is necessary since many crucial policies/decisions regarding public or individual health, environmental protection, and international trade are based on the results of analytical measurement.

However, CRMs with similar types of sample matrices have a high cost. Thus, at present, the requirements of CRMs keep growing. The increasing of the demand of CRMs are as a consequence of various factors such as for ensuring the performance of analytical equipment, the stricter of current regulations and the requirement for more accurate and reliable data in scientific and technological fields, and in the measurement related to the quality of life (Durbiano *et al.*, 2011). Indonesia is also experienced by this condition, and not yet established national chemistry metrology in Indonesia encourages us to develop a CRM of

coal fly ash. The development process of a CRM takes substantial time, effort, and required numerous data analysis (Park *et al.*, 2011). Reference material is material characterized by a metrologically valid procedure for one or more specified properties, sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.

The elemental characterization for assigning values of candidate reference materials is one of the most important steps in the development and production of a CRM. The certified values in a CRM are usually determined using a single primary method with confirmation by another method(s) or using two independent and critically evaluated methods (Gong *et al.*, 2014; Ohata & Miura, 2014; Park *et al.*, 2011). Potential primary methods that are generally used for the determination of trace elements in samples with complex matrices include neutron activation analysis (NAA) since the principle of NAA is well defined and all the parameters are understood (Miura, Chiba, & Kuroiwa, 2010; Park *et al.*, 2011).

NAA is well known as a non-destructive analytical method, basically free from a potential risk of loss and contamination during the sample preparation and measurement (Miura *et al.*, 2010). It is less strongly affected by the matrices of the sample because of the high penetration power of neutrons and gamma rays and is not affected by the chemical and physical states of the analyte elements (Kim, Lee, Hwang, Min, & Yim, 2013). Furthermore, Greenberg *et al.*, 2011, demonstrated that NAA could establish metrological traceability as a primary method of measurement (Greenberg, Bode, Nadai, & Bode, 2011). Therefore, the NAA method is expected to provide a very accurate result with a small bias, which is traceable to SI units.

In this study, NAA was used to characterize the coal fly ash candidate reference material that has been prepared. The sample weight optimization for NAA analysis was carried out and also it tested the homogeneity. The optimization, method validation, and comparison of NAA with other analytical techniques (e.g. XRF) were carried out to ensure valid, reliable, and accurate analytical methods to be applied for value assignment of reference material candidate of coal fly ash toward its certification.

2. BASIC THEORY

Neutron Activation Analysis

Neutron activation analysis (NAA) is a nuclear process used for determining the concentrations of elements in a vast amount of materials. NAA is significantly different from other spectroscopic analytical techniques in that it is based not on electronic transitions but nuclear transitions. NAA relies on excitation by neutrons so that the treated sample emits gamma-rays. It allows the precise identification and quantification of the elements, above all of the trace elements in the sample. NAA has applications in chemistry but also other research fields, such as geology, archeology, medicine, environmental monitoring, and even forensic science. (Greenberg *et al.*, 2011; Hamidatou, Slamene, Akhal, & Zouranen, 2013)

The sequence of events occurring during the most common type of nuclear reaction used for the NAA, namely the neutron capture or (n, gamma) reaction, is illustrated in Figure 1 (Hamidatou *et al.*, 2013). The creation of a compound nucleus forms in an excited state when a neutron interacts with the target nucleus via a non-elastic collision. The excitation energy of the compound nucleus is due to the binding energy of the neutron with the nucleus. The compound nucleus will almost instantaneously de-excite into a more stable configuration through the emission of one or more characteristic prompt gamma rays. In many cases, this new configuration yields a radioactive nucleus which also de-excites (or decays) by the emission of one or more characteristic delayed gamma rays, but at a much lower rate according to the unique half-life of the radioactive nucleus. Half-lives can range from fractions of a second to several years depending upon the particular radioactive species (Greenberg *et al.*, 2011; Hamidatou *et al.*, 2013).

NAA falls into two categories due to the time of measurement: (1) prompt gamma-ray neutron activation analysis (PGNAA), where measurements take place during irradiation, or (2) delayed gamma-ray neutron activation analysis (DGNAA), where the measurements follow radioactive decay. The DGNAA is a more common method used and generally called as NAA. About 70% of the elements have properties suitable for measurement by NAA. In most cases, the radioactive isotopes decay and emit beta particles accompanied by gamma-ray of characteristic energies, and the radiation can be used both to identify and accurately quantify the

elements of the sample. After irradiation, the samples can be measured instrumentally by a high-resolution semiconductor detector, or for better sensitivity, chemical separations can also be applied to reduce interferences. The qualitative characteristics are the energy of the emitted gamma-ray (E_γ) and the half-life of the nuclide ($T_{1/2}$), while for the quantitative characteristic is: the I_γ intensity, which is the number of gamma-ray of energy E_γ measured per unit time (Hamidatou *et al.*, 2013).

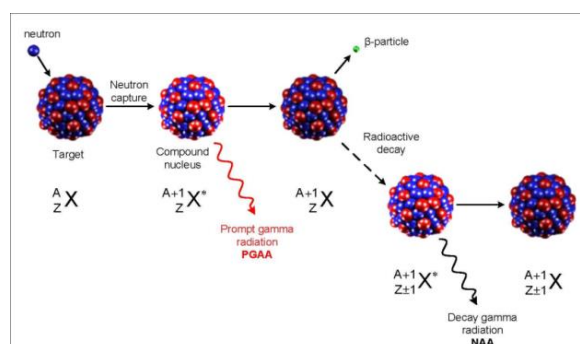


Figure 1 Diagram illustrating the process of neutron capture by a target nucleus (Hamidatou *et al.*, 2013).

Method Validation

Validation is confirmation through testing and providing objective evidence that certain requirements for a specific purpose are fulfilled. Validation of an analysis method needs to be done for non-standard methods, standard methods used outside its scope, and confirmation and modification of standard methods to confirm that the method is suitable for the intended use. Method validation parameters in this activity include accuracy and precision. Accuracy is a match between the results of the analysis with the true value and expressed in %recovery (%R) obtained through the equation:

$$\%R = \frac{X_{test}}{X_{sert}} \times 100\% \quad (1)$$

Where,

X_{test} : analytical result

X_{sert} : certificate value of the element observed

Precision is expressed as coefficient of variation (% KV) or a relative standard deviation (RSD) expressed in the following equation:

$$RSD = \frac{SD}{\bar{x}} \times 100\% \quad (2)$$

Where:

- SD : the standard deviation of the analytical results
 X : the average of the analytical results

3. METHODS

3.1. Preparations of coal fly ash reference material candidate.

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 was used to produce the reference material candidate. The reference material candidate was prepared according to the ISO Guide 35 [(ISO, 2006)]. The bulk material was dried in the closed cabinet, heated by an infrared lamp with temperature set not more than 50°C for 3 days. The dried coal fly ash was ground 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, 1000mL). Several sub-samples were taken from bulk containers for the preliminary study of homogeneity. After a satisfactory level of homogeneity was achieved, the coal fly ash than was distributed representatively into a 60 mL capacity of high-density polyethylene bottles. Approximately 50 gr of the material was transferred to each bottle. A total of more than 150 bottles were then labeled with the name of the material and serial number. The bottles were kept in dry cabinet storage.

3.2. Samples and standards preparation for INAA Analysis.

For optimization of sample weight for analysis, 25, 100, and 250 mg taken from 10 bottles of candidate RMs and placed in the 0.3 mL polyethylene vials for 25 and 100 mg samples and 0.5 mL polyethylene vials for 250 mg samples. The vials were then sealed. SRM NIST 1633b Coal Fly Ash that was used for quality

control analysis was weighed about 50 mg and placed in the 0.3 mL polyethylene vials also. This SRM were prepared for six replicates. The E-Merck certified standard solutions of multi-elemental were used for this INAA analysis. The standard solutions were taken quantitatively by pipetting 100 µL to 0.3 mL polyethylene vials and then were air-dried under the heat of infrared lamps. The vials were then sealed.

3.3. Irradiation and Counting for INAA Analysis

The samples, SRMs, and standards were irradiated in the rabbit system of The Multi-Purpose Reactor G.A Siwabessy with neutron flux ~1013 n.cm⁻².s⁻¹. Short, medium and long irradiations were performed to determine various radionuclides with different half-lives. The short-lived nuclides were irradiated for the 60s, while for the medium-lived and long-lived nuclides were irradiated for 600s and 2h respectively. After 5 minutes of cooling, the short-lived nuclides were counted for about 300s. While for medium-lived nuclides counted for 2000-3000s after 1-day cooling, and long-live nuclides were counted for 5000-10000s after one-week cooling. The gamma counting was carried out using a gamma spectrometer with an HPGe detector. All of the samples, SRM and standard were counted at the same position and distance from the detector to minimize errors due to differences in counting geometry. The measured gamma-ray spectrum was analyzed by using software GENIE 2000. The Instrumental Neutron Activation Analysis with a relative method was carried out for determining the elemental concentration of the samples.

3.4. Elemental characterization using XRF

About each of 2 g taken from more than 6 bottles of candidate RMs then pressed and placed in the polyethylene sample holder covering with Mylar. SRM NIST 1633c Coal Fly Ash that was used for quality control analysis was weighed about 2 g and then pressed and placed in the polyethylene sample holder covering with Mylar.

Table 1 Measurement application condition of XRF.

Condition name	kV	uA	Filter	Medium	Time of meas.(s)
<Cd-Sm>	30	300	Ag	Air	300
<Cl-V>	14	300	Al_thin	Air	200
<Cr-Co>	20	300	Al	Air	200

Condition name	kV	uA	Filter	Medium	Time of meas.(s)
<Na-S>	11	200	<none>	Helium	300
<Ni-Ag>	30	300	Mo	Air	300

Table 2 Analytical results of elements in the coal fly ash samples of various of sample weights by NAA (mean ± standard deviation, n = 10).

Element	Unit	Sample weight (mg)		
		25	100	250
As	mg/kg	19.7 ± 2.12	19.5 ± 0.91	16.8 ± 1.20
Co	mg/kg	59.6 ± 3.86	59.7 ± 2.55	52.1 ± 3.15
Cr	mg/kg	100.2 ± 4.7	93.2 ± 4.1	82.7 ± 10.6
Fe	% wt	8.91 ± 0.39	8.74 ± 0.43	7.41 ± 0.26
K	% wt	0.62 ± 0.03	0.55 ± 0.04	0.47 ± 0.05
La	mg/kg	45.7 ± 3.4	44.3 ± 1.7	41.7 ± 1.4
Mn	mg/kg	990 ± 32.3	967 ± 31.3	n.a
Na	% wt	0.96 ± 0.05	0.87 ± 0.05	0.67 ± 0.08
Th	mg/kg	15.4 ± 0.8	15.4 ± 0.8	12.8 ± 1.2
Zn	mg/kg	274.9 ± 7.0	268.3 ± 6.5	268.3 ± 15.1
Al	% wt	11.08 ± 0.57	n.a	n.a
Ca	% wt	4.23 ± 0.41	n.a	n.a

n.a: not analyzed

also. The standards used for XRF analysis are NIST SRM 1633b Coal Fly Ash, NIST SRM 1632 Coal, NIST SRM 2711 Montana Soil and IAEA RM SL-1 Soil were prepared in the same way as the samples and placed in the same size sample holders. The application conditions of measurement were described in Table 1

4. RESULTS AND DISCUSSIONS

4.1. The optimization of sample weight for NAA analysis

The optimization of sample analysis using NAA was carried out with varying sample weights. This would give an optimum sample weight that will have better results. This will also evaluate the minimum mass that allows the quantification of all elements investigated in this study. Samples with various masses, which are 25, 100, and 250 mg, from the same bottle were evaluated. Each sample weight was taken for 10 replicates. All replicates of all sample weight were measure twice. The analytical results of samples with different sample weights were listed in Table 2. The homogeneity of each sample weight was also observed. Analysis of Variance (ANOVA) was applied to execute the homogeneity test at a 5% significance level [19].

This statistical test is recommended by ISO Guide 35 and is also conventionally utilized of most work related to the preparation of a CRM (Maria *et al.*, 2015). The results of the homogeneity test were presented in Table 3.

Table 2 showed that there are some differences between results among all sample's weight, especially for 250 mg samples weight. On sample weight of 250 mg showed a decrease of concentration value. This is because of the characteristic of the research nuclear reactor that has been used for the NAA analysis. The high flux of neutron gave the gamma radiation intensities quite high. Therefore, made the samples were not allowed to get out of the lead glass box of irradiation facilities because of the high rate of radioactivity due to safety and protective radiation reason. For this condition, the samples experienced the cooling time that quite long for short-lived nuclides such as; Al, Ca, and Mn, which are unsatisfactory to be analyzed. While for the medium and long-lived nuclide, the samples tend to have higher dead time, and this made the measurement was not optimized yet for the 250 mg of the sample weight.

Another optimum condition for the 250 mg sample weight must be further investigated.

For the same reason for radiation safety, the Al and Ca elemental analysis of the 100 mg samples cannot be carried out due to the high rate of the gamma decay rate. Among the results of 25 and 100 mg of samples weight mostly was not significant differences. However, higher

standard deviations were observed for sample weight of 25 mg even though they are still in acceptable criteria of standard deviation set by our laboratory, $\leq 10\%$ for major concentrations, and $\leq 20\%$ for minor and trace concentrations.

Table 3 ANOVA results for the study the homogeneity of the coal fly ash candidate reference material for sample weights of 25, 100 and 250 mg.

Element	F_{crit} (n=10)	Sample weight (mg)					
		25		100		250	
		F_{calc}	p_{value}	F_{calc}	p_{value}	F_{calc}	p_{value}
As	3.020	2.410	0.093	1.036	0.474	1.578	0.243
Co	3.020	2.923	0.055	0.895	0.561	0.934	0.536
Cr	3.020	2.665	0.071	1.084	0.447	1.831	0.180
Fe	3.020	0.534	0.820	1.621	0.231	1.537	0.256
K	3.020	0.567	0.797	1.669	0.218	1.745	0.199
La	3.020	2.809	0.062	0.928	0.540	0.979	0.508
Mn	3.020	2.377	0.097	1.326	0.332	n.a	
Na	3.020	2.873	0.058	2.226	0.114	2.621	0.075
Th	3.020	0.775	0.644	1.628	0.229	1.852	0.175
Zn	3.020	2.590	0.077	1.453	0.284	1.629	0.229
Al	3.020	2.063	0.137	n.a		n.a	
Ca	3.020	1.283	0.350	n.a		n.a	

n.a: not analyzed

The homogeneity of the elements As, Co, Cr, Fe, K, La, Mn, Na, Th, and Zn of each sample weights was evaluated by comparing the variances obtained in the between-bottle test with the F-critical values [20]. Table 3 showed that the F-calculated values for all elements of each sample weights were less than the F-critical value of 3.02 at a 5% significance level, demonstrating that there are no significant differences between variances obtained using all sample weights of 25, 100 and 250 mg for mostly elements observed. For short-lived nuclides, due to a high rate of radioactivity occurred for 100 and 250 mg of sample weight that unable to be well quantified, homogeneity was assessed for 25 mg of the sample weight. However, for this study, based on the results presented in Table 2 and 3, a sample weight of 100 mg was best chosen for further studies in ensuring the robustness of the used analytical method especially for medium-long lived nuclides while for short-lived nuclides, such as Al and Ca, the weight of 25 mg was optimum to be analyzed by NAA using a typical nuclear reactor with the high flux of neutron.

4.2. Validation of NAA analytical method used for elemental characterization

Some analytical parameters were evaluated for the validation process of the method used for the quantification of the elements. The precision of the method was evaluated as a relative standard deviation (RSD) from 16 elements (n=6). The accuracy of the method used was confirmed by analyzing the coal fly ash certified reference material (NIST 1633b) furnished by the National Institute of Standards and Technology (Gaithersburg, MD, USA). The analysis of this CRM was performed using the same procedure as applied for the coal fly ash samples. The measure values of NIST 1633b are given in Table 4.

The concentrations of all elements are consistently within the uncertainties range of the certified value as shown in Table 4. It can be seen also that the accuracy the analytical method observed is quite good with %recovery value in the range of 90-110% which means that the analytical method has little bias, less than 10%. The precision of the analytical method was expressed by RSD. The results were in the range of 1.8 – 8.3 %. These results of precisions

showed good repeatability, but it will give a meaningful contribution to the uncertainty budget of the candidate reference material. The uncertainty of reference material is generally contributed from the characterization of the analytical method, the homogeneity of reference material developed, and its stability including the short and the long term of stability as described in Figure S1. Repeatability will be affected not only in the uncertainty budget from characterization but also from stability as well. According to Miura et. al, 2010, NAA sometimes shows a large measurement uncertainty

compared with other analytical methods, and the main components of measurement uncertainty of NAA are those associated with corrections for the difference of neutron flux among samples and comparator standards, thus also affected to the sample-to-sample repeatability (Miura *et al.*, 2010). However, it can be reduced by applying an internal standard method to NAA (Miura *et al.*, 2010). In conclusion, NAA as observed analytical method were successful for the determination of multi-elements in coal fly ash.

Table 4 Analytical results, accuracy (%Recovery) and precision (RSD) of NAA analysis of coal fly ash CRM (NIST 1633b).

Element	Unit	Mass Fraction		%Recovery	RSD
		Analytical Result	Certified value		
Al	%	13.37 ± 0.24	13.28 ± 0.61	100.7	1.82
As	mg/kg	183 ± 6.2	186.2 ± 3	98.2	3.40
Ba	mg/kg	724 ± 42	709 ± 27	102.1	5.80
Fe	%	7.65 ± 0.25	7.78 ± 0.23	98.3	3.25
K	%	1.785 ± 0.0727	1.773 ± 0.066	100.7	4.07
Ca	%	1.36 ± 0.034	1.365 ± 0.04	99.8	2.47
Co	mg/kg	49.6 ± 2.3	50	99.1	4.59
Cr	mg/kg	188 ± 11.8	198.2 ± 4.7	95.1	6.24
La	mg/kg	87.1 ± 3.5	87 ± 2.6	100.1	4.02
Mg	%	0.506 ± 0.023	0.498 ± 0.052	101.6	4.64
Mn	mg/kg	237 ± 12	240 ± 3.4	98.6	5.07
Na	mg/kg	1715 ± 75	1707 ± 59	100.5	4.37
Zn	mg/kg	222 ± 12	210	105.7	8.26
Th	mg/kg	24.9 ± 1.4	25.7 ± 1.3	96.8	5.43
Ti	%	0.728 ± 0.025	0.724 ± 0.03	100.6	3.44
V	mg/kg	269 ± 14.1	286.2 ± 7.9	94.0	5.24

4.3. Comparison of the analytical results between NAA and XRF methods.

To ensure the reproducibility of the NAA analytical method and also the robustness of the method, a comparison test was carried out. Several samples of coal fly ash candidate reference materials were analyzed using two analytical methods which are NAA and XRF. XRF was one of the advanced analytical methods that are also multi-elements and non-destructive. Besides confirming the accuracy of the NAA method observed, this comparison was

also useful to complement both analytical methods. However, the comparison test should be done after ensuring the accuracy of the analytical methods compared. To fulfill this requirement, quality assurance of the XRF analytical method was applied using CRM of coal fly ash (NIST 1633b) that were analyzed in the same experimental conditions that are used for sample analysis. Several elements in that CRM were detected and the results were then compared with its certificate values. The ratio of mean value between the analysis results obtained with the XRF method and the certificate

values were shown in Figure 2. Figure 2 showed that the ratio was in the range of 0.94 – 1.06. The concentration of most elements analyzed is consistently within the uncertainties of the certified value, and therefore XRF method quite accurate. As much as 6 samples of coal fly ash were used to be analyzed with NAA and XRF methods. The comparison was carried out for 16 elements [RD1] [ED2] which are Al, As, Ba, Ca, Co, Cr, Fe, K, La, Mn, Sr, Th, U, V, and Zn. Lead

(Pb) cannot be compared since Pb has physical properties of small neutron activation cross-section that made it difficult to be activated by neutron and analyzed by NAA. For this reason, Pb is also effective to be used as gamma radiation shielding. The comparison results between NAA and XRF are presented by plotting the results on regression linear as described in Figure 3.

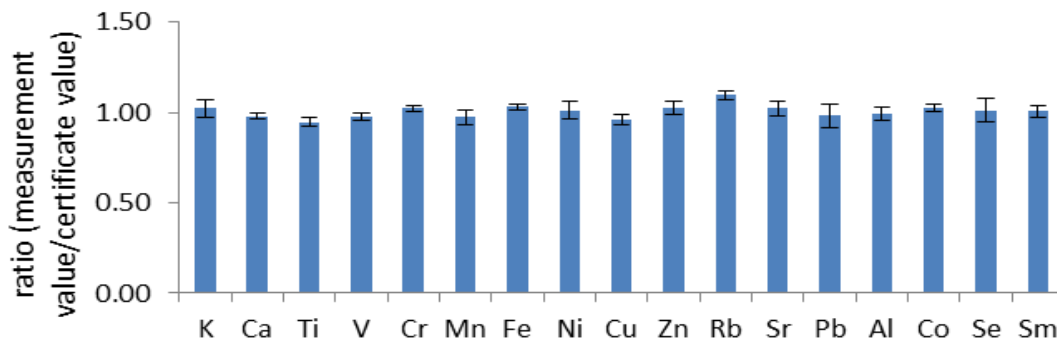


Figure 2 Ratio of mean value of measurement/certificate of CRM coal fly ash (NIST 1633b) by XRF method.

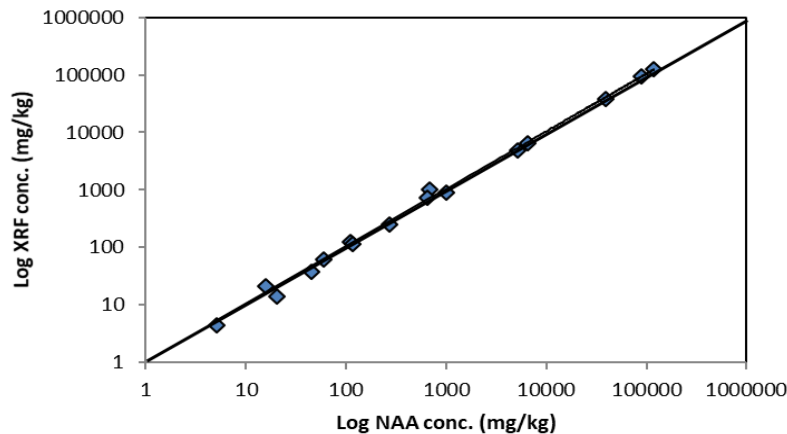


Figure 3 The comparison of elemental concentrations obtained from NAA and XRF analytical methods.

From Figure 3, it can be shown that the comparison of NAA and XRF are having a good agreement with each other, as it can be seen that the most of the data plotted along $x = y$ line. Several studies reported the comparison results of two analytical methods using the scatter plot on regression linear, visualization of the data facilitate agreement/disagreement of the data which then can be proved statistically using

significance difference test (Du *et al.*, 2013; Gemayel *et al.*, 2017; Kodamatani *et al.*, 2017). This showed that the NAA method has good reproducibility and in confirm with the XRF method. Either NAA or XRF method could be a substitute and also complement analytical methods of each other. In a CRM development, the assignment of value of candidate reference material could be determined using a single

primary method with confirmation by another method(s) or using two independent and critically evaluated methods (Park *et al.*, 2011). These results showed that the NAA method is capable to determine the assigned value of coal fly ash candidate reference material. For characterization of elements in coal fly ash candidate reference material, an XRF method may also be used, since those two methods complement one other by each compensating for the weaknesses of the other method. Thus, the certified values obtained from the candidate reference materials will be more comprehensive and reliable. However, a further study regarding the uncertainty budget of the NAA and other methods complied are still need to be done toward certification of the coal fly ash candidate reference material that being developed. This study is hoped to be one meaning step of many steps that must be fulfilling for the development of qualified certified reference materials in Indonesia.

5. CONCLUSION

The NAA method with the applied procedure in this study successfully achieved a valid and accurate elemental characterization in coal fly ash reference material candidate. A 100 mg samples weight was taken as a minimum sample intake for NAA analysis of coal fly ash that has good results and the homogeneity of the sample is still assured. Because the NAA gave the consistent analytical results with the certified value of NIST 1633b through method validation which is tested its accuracy and precision, shown by 94-106 %recovery and <10% RSD; and it is also showed excellent agreement of analytical result compared to that obtained by the XRF method, thus the NAA method could be evaluated as valid and reliable analytical method for the elemental characterization of coal fly ash and is able to assign the elemental value toward the certification of the coal fly ash reference material candidate that will be useful CRM for the development of chemical metrology in Indonesia.

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