

## Comparison of NAA XRF and ICP-OES Methods on Analysis of Heavy Metals in Coals and Combustion Residues

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Received January 5, 2017; Accepted April 20, 2017

### ABSTRACT

Heavy metals in the samples of coals and combustion residues (bottom ash and fly ash) from Pacitan coal-fired power plant (CPP) have been identified by using NAA, XRF, and ICP-OES methods. This research was aimed to understand the analysis results correlation coefficient ( $R$ ) and determine the enrichment ratio ( $ER$ ) value of the samples by using three analysis methods. The results showed 10 elements have been simultaneously detected in all samples. The correlation coefficient of analysis results of metals content in coals by using NAA-XRF, XRF-ICP OES and with ICPOES-NAA methods gives  $R^2 \leq 1$  respectively. The correlation coefficient of analysis results of metals content in bottom ash and fly ash by using the methods of NAA-XRF, XRF-ICPOES, and ICPOES-NAA gained  $R^2 \approx 1$  respectively. ICP-OES method was most satisfactory in this study. The value of  $ER$  for identified metals by using the three methods in the samples of bottom ash and fly ash yielded the value over one, and  $ER$  value of fly ash was greater in comparison to the bottom ash.

**Keywords:** bottom ash; fly ash; NAA; XRF; ICP-OES

### ABSTRAK

Logam berat dalam sampel batubara dan residu pembakaran batubara (bottom ash dan fly ash) dari PLTU Pacitan telah diidentifikasi dengan menggunakan metode NAA, XRF, dan ICP-OES. Penelitian ini bertujuan untuk mengetahui koefisien korelasi ( $R$ ) hasil analisis dan menentukan nilai Enrichment Ratio ( $ER$ ) pada sampel batubara, bottom ash dan fly ash dari ketiga metode analisis. Hasil penelitian menunjukkan telah terdeteksi serentak 10 unsur dalam semua sampel. Koefisien korelasi hasil analisis kandungan logam dalam batubara menggunakan metode NAA-XRF, XRF-ICPOES dan dengan ICPOES-NAA masing-masing diperoleh  $R^2 \leq 1$ . Sementara koefisien korelasi hasil analisis kandungan logam dalam bottom ash dan fly ash dengan metode NAA-XRF, XRF-ICP-OES, dan ICPOES-NAA masing-masing diperoleh  $R^2 \approx 1$ . ICP-OES adalah metode analisis paling memuaskan dalam studi ini. Nilai  $ER$  untuk logam yang diidentifikasi dengan menggunakan ketiga metode pada sampel bottom ash dan fly ash menghasilkan nilai lebih besar dari satu, dan nilai  $ER$  pada fly ash lebih besar dibandingkan dengan bottom ash.

**Kata Kunci:** bottom ash; fly ash; NAA; XRF; ICP-OES

### INTRODUCTION

The combustion process of coals at coal-fired power plant (CPP) produces waste in the form of coal ash at the sum of 2-10%. Coal ash is composed of two types of bottom ash and fly ash. Fly ash is a major part of the coal ash that is 80%. Coal ash contains various kinds of metals. They are metals that can be recovered as Fe, Al and Ca [1]. In addition, it is also indicated that coal ash contains toxic heavy metals, such as Pb, Cr, Cu, Ni, and Cd [2]. State Minister of Life Environmental (KNLH) stated that ash produced from coals combustion product is included in the hazardous and toxic wastes

under Government Rule No.85 of 1999 on Amendment to Government Regulation No. 18 Year 1999 on the management of hazardous and toxic wastes [3].

Concentration of major, minor, and trace elements in the coals were very extremely varying and depends on the type as well as coals composition, condition during the combustion, and the efficiency of instrumental control quality [4]. The quality of fly ash and bottom ash was determined from the chemical composition of coals and combustion parameter. Therefore, it is important to the analyze chemical composition of coals together with bottom ash and fly ash, for example by means of multi elements methods

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and simultaneously such as neutron activation analysis (NAA), x-ray fluorescence (XRF) etc., that elemental pathway to the environment could be predicted.

Multi elements technical analysis such as NAA, XRF, and inductively-coupled-plasma-optical-emission-spectroscopy (ICP-OES) were capable for analyzing the elements in the various matrixes of solid sample and they were widely used. Some techniques are used in the analysis each of which has advantages and its disadvantages. Application technique of NAA has its advantages, among of which are multi elements, non-destructive, sensitive, highly selective, the detection limits reaches the nanogram order for the certain elements. This technique also capable in the samples analyzing at the tiny weight of ~0.010 g, the samples to be analyzed could be in the forms of solid (rigid, granular), paste, as well as liquid, and the samples was not easily contaminated after neutron activation. Whereas, ICP-OES technique is a technique enable to analyze the major, minor, and trace elements in the environmental samples. This technique is benefiting of long linear range, highly precision, lower detection limits even down to ppb level, but this technique is destructive technique, so it needs the longer preparation time [5]. Furthermore, the analysis technique that is ordinarily used in the coals laboratory is XRF. This technique needs a cheaper expense and faster compared to NAA and ICP-OES techniques, because it has an easy way of preparing the samples. The sample forms could be solid (granular, massive), paste as well as liquid, non-destructive, as well as an easy way of calibrating. In spite of the advantages mentioned above, XRF technique has a disadvantage in performance, that is, it is influenced by sample matrix and standard, and also needs the different excitation sources (radio isotope) for some elements [6]. The different techniques were used in characterizing coals, bottom ash and fly ash to give an evaluation when one method with others have lacking in determining an element composition.

Patra et al. [7] stated that there are about 16 elements that could be analyzed in the coals, bottom ash, and fly ash by Particle induced X-ray emission spectroscopic (PIXE) which contains major, minor and trace elements. Concentration of heavy metals elements such as Co, Ni, Cu, Zn, Rb, Sr, and Pb in the samples of Indian coals they were detected in low concentration namely between 2.5–4.2 ppm and for Fe and Ti elements were in an adequate highly concentration of 0.33% and 0.15%.

Lim et al. [8] in his research on coals field and its combustion residue at Korea CPP could be determined total content of 31 major to trace elements which could be analyzed using NAA methods accurately. It was

reported that fly ash and bottom ash contain higher concentration compared to that of coals.

Considering the lack of information about the total concentration of elements in coals and coals-residue in Indonesia, this investigation aims at providing the intended information data, by identifying the heavy metals content in the coals and coals residue, by using three instrumental analysis techniques of NAA, XRF, and ICP-OES; finding the correlation coefficient (R) of metals content analysis results by those three methods; as well as determining Enrichment Ratio (ER) for metals content in the bottom ash and fly ash from Pacitan CPP.

## EXPERIMENTAL SECTION

### Sampling

Samples of coal, bottom ash and fly ash were taken directly at the Pacitan CPP, Sukorejo, District of Sudimoro, Pacitan, East Java, Indonesia on October 20-21, 2014 at the sum of  $\pm 5$  kg respectively.

### Sample Preparation

Samples of coal, bottom ash and fly ash were finely pound and sieved to pass 170 mesh. After sieved, the samples were then homogenized and determined their water content. Finally, they were inserted into the glass bottle and put in the desiccator.

### Secondary Standard Preparation

The use of NAA and XRF methods in this study with the relative technique, namely using an artificial reference standard (secondary standard A and B). Secondary standard of dry mixture A (for coal analysis) and B (for analysis of fly ash and bottom ash). Standard A was made of the solution of 10 elements of liquid standard of Merck, was taken at the amount of 0.10-0.50 mL, mixed and dried with a heating lamp in a 0.5 mL pp vial. Standard B was made of the solution of 10 liquid standard elements of Merck, was taken at the amount of 0.04-7.3 mL, mixed and dried with a heating lamp in a 0.5 mL pp vial.

### Homogeneity Test

Samples of coal, bottom ash and fly ash that has passed 170 mesh and homogenized, were put into the high density polyethylene bottles (HDPE), at the sum of 10 random packing, and the elements of Fe and Sr were analyzed in duplicate by using XRF instrument [9].

### Sample Analysis Using XRF Method

Samples of coal, bottom ash and fly ash that has been prepared and homogenized, weighed of  $\pm 5$  g were put into the polyethylene (PE) bottle lining by mylar plastic, then were analyzed by referring to [10].

### Sample Analysis by Using NAA Method

Homogenized samples of coal, bottom ash and fly ash were weighed of  $\pm 0.10$  g, put in a 0.5 mL polyethylene vial then glued (glass stirrer was heated with a Bunsen burner). The same matter was done at 0.10 g SRM NIST 1632d Bituminous Coal and 0.10 g SRM NIST 1633c Coal Fly Ash. Subsequently the samples, the secondary standard, primary standard primer (NIST 1632d and NIST 1633c), and blanks were put into the cladding and be ready for being irradiated. The samples were irradiated at the Pneumatic facility for 5 min for a short irradiation and Lazy Susan for  $2 \times 6$  h for medium and long irradiation with a neutrons flux of  $\sim 10^{11}$  n.cm<sup>-2</sup>.s<sup>-1</sup> and a power of 100 kW.

Furthermore, the samples, the primary standard, secondary standard, and the blanks were removed then replaced with a new plastic clip. Then they were cooled for 5 min for a short-life, 7 days for middle-life and 20 days for long-life. Furthermore, they were counted in accordance with their half-life (depending on the type of the element being analyzed) where short irradiation (an element of short half-life) was counted for 600 sec, medium irradiation (elements in the medium half-life) was counted for 1000 sec and long irradiation (element of long half-life) was counted for 3600 sec with gamma spectrometer equipped with HPGe detector. After the counting stopped, the results obtained were processed using the software of Genie 2000.

### Sample Analysis by Using ICP-OES method

Elemental analysis of Al, K, Na, Fe, Ti, Sr, Ba prepared to ASTM D 6349-13 [11] and the elements of Co, Cr, Cd, Zn, La followed to ASTM D 6357-11 [12] on a sample of coal, fly ash and bottom ash.

## RESULT AND DISCUSSION

In this study, it has been conducted a water concentration test (by gravimetric), homogeneity test (major and minor elements by using XRF and single factor ANOVA), the methods validation of XRF and NAA with SRM NIST 1632d Bituminous Coal and SRM NIST 1633c Coal Fly ash, the elemental composition test in coal, bottom ash and fly ash by using three techniques of analysis namely, NAA, XRF, and ICP-OES.

### Homogeneity Test

The method of XRF was selected in homogeneity test because it is a cheaper method, fast and easy in the sample preparation. In this homogeneity test, it was only Fe element that was analyzed (representing the major elements) and Sr element (representing the minor elements) in the samples that was being analyzed so it would be known whether from both elements detected in samples of coal, bottom ash and fly ash has been homogenous. The homogeneity test criteria used in the criterion 1, namely if  $F_{\text{counting}} < F_{\text{table}}$  then the sample was mentioned to be homogeneous. The value of F was gained from critical table with the confident level of 95% [9]. Results of homogeneity test samples of coal, bottom ash and fly ash are shown in Table 1.

The results of the  $F_{\text{test}}$  for the homogeneity test (Table 1) using criteria 1 with a 95% confidence level showed that  $F_{\text{arithmetic}}$  for samples of coal, bottom ash and fly ash were in the range of 0.673 to 2.805  $< F_{\text{table}}$  (3.020). This matter indicates that the sample has been homogenized, so it can be proceed for the analysis of the chemical composition of the sample.

### Validation of Analysis Methods

To ensure the quality of the analysis data (QA) of the analysis results, the NAA and XRF analysis methods used validation was prior to be conducted by looking at the accuracy value. Accuracy can be calculated from the comparison of the elements concentration in the measurement results of SRM and in the certificate of SRM. Validation methods have been made by means of testing of SRM NIST 1632d Bituminous-Coal and SRM NIST 1633c Coal Fly ash having matrix similar to the samples, with the data shown in Table 2 and Table 3.

The analysis results at SRM NIST 1633d (Table 2) certificate shows that the range of percentage accuracy for NAA method ranged from 91.23%-113.8% and XRF methods ranged from 92.8%-104.76%. Likewise, the measurement accuracy of certificate of NIST SRM 1633c (Table 3) ranged between 91.78%-110.28% for NAA method and between 95.61%-103.63% for XRF method.

Table 2 and Table 3 showed that there is a good value conformity between the measurement of using NAA and XRF with the value of the certificate. This matter is in accordance with the acceptance limits of accuracy based on Association of Official Agricultural Chemist (AOAC), namely to the concentration range of 10;1; and 0.1%, respectively by 95-102%, 92-105% and 90-108% [13], wherein both of the test methods used has high accuracy and can be used for the

**Table 1.** Determination of F test samples of coal, bottom-ash, and fly-ash using XRF

Results of F test					
Elements	Coal	Bottom-ash	Fly-ash	F Table	Description 95%
Fe	1.295	0.673	1.971	3.020	$F_{arithmetic} < F_{table}$
Sr	1.854	2.805	2.089		

**Table 2.** Accuracy of SRM NIST 1632d Bituminous coal using NAA and XRF methods

Element	Certificate Value of SRM NIST 1632d		Analysis Results of NAA			Analysis Results of XRF		
	Concentration (mg.kg <sup>-1</sup> )		Concentration (mg/kg)		Accuracy (%)	Concentration (mg.kg <sup>-1</sup> )		Accuracy (%)
Al	9100.00 ± 50.00		8900.00 ± 3200.00		97.75	NA		
Fe	7500.00 ± 200.00		7400.00 ± 490000.00		98.67	7100.00 ± 300.00		94.67
Ti	477.00 ± 10.00		476.00 ± 7.11		99.79	482.00 ± 6100.00		101.05
Ba	40.40 ± 0.89		39.83 ± 0.82		98.54	41.70 ± 0.11		103.14
Sr	63.50		67.89 ± 10.48		106.91	66.50 ± 4.81		104.76
Cr	13.70		12.73 ± 0.09		92.92	NA		
La	5.00		5.69 ± 0.01		113.80	4.64 ± 0.13		92.80
Zn	12.90		13.33 ± 2.91		103.33	12.20 ± 2.11		94.81
Co	3.42 ± 0.05		3.12 ± 0.11		91.23	NA		
Cd	0.08 ± 0.01		0.08 ± 0.02		100.00	NA		

NA = not-analyzed

**Table 3.** Accuracy of SRM NIST 1632c Coal fly ash using NAA and XRF methods

Element	Certificate Value of SRM NIST 1632c		Analysis Results of NAA			Analysis Results of XRF		
	Concentration (mg.kg <sup>-1</sup> )		Concentration (mg.kg <sup>-1</sup> )		Accuracy (%)	Concentration (mg.kg <sup>-1</sup> )		Accuracy (%)
Al	132800.00 ± 6100.00		131500.00 ± 0.30		99.02	NA		
Fe	104900.00 ± 3900.00		104800.00 ± 200.00		99.90	100300.00 ± 4700.00		95.61
Ti	7330.00		7300.00 ± 260700.00		100.00	7100.00 ± 3700.00		97.20
Ba	1120.00 ± 33.00		1170.00 ± 20600.00		104.78	1100.00 ± 900.00		100.00
Sr	901.00 ± 56.00		894.35 ± 53.49		99.26	904.24 ± 52.53		100.35
Cr	258.00 ± 6.00		260.49 ± 0.72		99.03	NA		
La	87.00 ± 2.60		78.05 ± 0.08		110.28	90.16 ± 0.05		103.63
Zn	235.00		215.70 ± 24.48		91.78	NA		
Co	42.90 ± 3.50		43.35 ± 0.48		101.05	NA		
Cd	0.76 ± 0.01		0.79 ± 0.27		103.69	NA		

NA= not-analyzed

analysis of metals in samples of coal, bottom ash and fly ash.

### Analysis of Coal

Analysis of samples of Pacitan CPP was done using three methods namely NAA, XRF and ICP-OES. The analysis results of coal samples detected some elements of major, minor and trace, have been 10 elements, namely Al, Fe, Ti, Ba, Sr, Zn, Cr, Co, La, and Cd will be discussed. The average concentration of the identified elements in the coal are shown in Table 4.

Table 4 shows that the relative abundance of the elements in the coal using 3 methods obtained the elements Al > Fe > Ti > Ba > Sr > Cr > La > Zn > Co > Cd. The order of element concentrations obtained in the coal being analyzed resembles a sequence of metallic elements found in the samples crust of the earth,

because coal is the material that is formed from the higher plants residue buried under layers of earth millions of years, so that the elements contained in the coal is not different much from the constituent elements in the earth's crust.

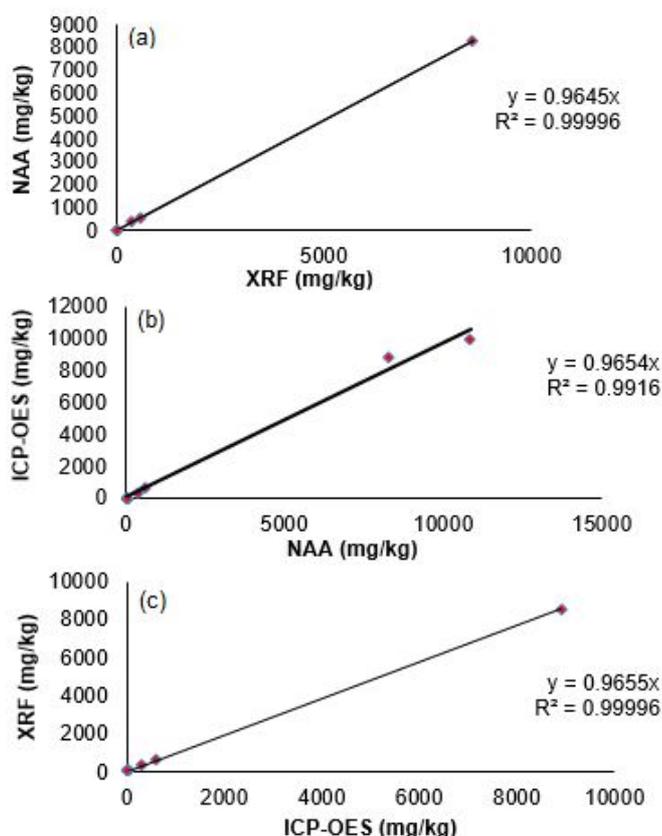
The results of analysis by using three methods showed that the elements of Al and Fe are found most abundantly were included into the two major elements, high concentration of Al at a guess was derived from clay minerals whereas Fe element derived from the pyrite and jarolite mineral. The elements of Ti, Ba, Sr, Cr, La, Zn, Co, and Cd found in low concentrations are expressed as minor elements and trace element.

Coal analysis results obtained in line with research conducted by Tiwari et al. [6] using EDXRF which resulted in the relative abundance of the elements in the coal were Si > Al > Fe > Ca > Mg > K > Na > Sr > V > Zn > Mn > Cr > Cu > Pb > Ni > Co > Al > Cd,

**Table 4.** Metal concentration in coals using three methods

Element	NAA		XRF		ICP-OES	Unit
Al	10900.00	± 2000.00	NA		990.00	mg.kg <sup>-1</sup>
Fe	8300.00	± 52.35	8700.00	± 170.00	8900.00	mg.kg <sup>-1</sup>
Ti	613.71	± 8.75	600.42	± 12.41	600.00	mg.kg <sup>-1</sup>
Ba	332.01	± 0.93	341.66	± 0.99	333.48	mg.kg <sup>-1</sup>
Sr	45.36	± 13.83	45.02		45.28	mg.kg <sup>-1</sup>
Zn	15.26	± 2.70	17.24		17.77	mg.kg <sup>-1</sup>
Cr	23.80	± 0.21	NA		22.18	mg.kg <sup>-1</sup>
Co	3.19	± 0.12	NA		3.13	mg.kg <sup>-1</sup>
La	18.98	± 1.07	20.82		19.42	mg.kg <sup>-1</sup>
Cd	0.78	± 0.10	NA		0.75	mg.kg <sup>-1</sup>

NA = not analyzed

**Fig 1.** Comparison the element concentration in coals sample obtained by using (a) NAA vs. XRF, (b) ICP-OES vs. NAA, (c) XRF vs. ICP-OES

where the concentration of Al found was most abundantly after Si which ranges from 3.21% and Cd found in coal was the least that was only about 0.37 mg/kg. Research conducted by Sutcu and Karagiyit [14] stated that the main elements such as Al and Fe from the coal sample were mostly associated with silicates and carbonate minerals. Al and Fe were associated with feldspar, quartz and clay mineral. Highly concentration of Al deriving from clay mineral and feldspar whereas Fe element derived from the minerals of pyrite, jarolite, and clay.

The analysis results of minor elements and trace element content of coal Pacitan power plant in Table 4 when compared with worldwide coal deposits reported by Ketris [15], Wang [16], Meravi [17], and Ghodke [18] stated that the range concentration of Cr was (1 to 61), Sr (110), Co (5.1), Zn (23), and Cd (0.01 to 1) mg/kg. Related to minor and trace element concentrations in the coal studied, the element content of coal Pacitan power plant was in the lower range compared to the average concentration of the element content of coal worldwide. This indicates that the kind and the type of coal used each country will produce the different element content.

The analysis results of elemental concentrations of Al, Ti, Sr, Cr, Co, and Cd in coal using NAA method was higher than that of XRF and ICP-OES while for the elements of Fe, Ba, Zn, and La was lower than the other two methods. Overall the analysis results obtained using the three methods were well correlated. The analysis results of coal of these three methods compared to plotting those three methods provides slope and linear regression approaches a value of 1, which was shown in Fig. 1.

Fig. 1 showed that comparison of the analysis results of the coal by using NAA and XRF gave the slope = 0.9645 and the correlation coefficient ( $R^2$ ) = 0.99996. Comparison of the analysis results of coal between ICP-OES versus NAA gave the slope = 0.9654 and  $R^2$  = 0.9916. As for the results of the XRF versus ICP-OES gave the slope = 0.9665 and  $R^2$  was 0.99996. The analysis result of the of coal using NAA, XRF and ICP-OES methods have a good relationship with each other in giving the analytical results. The study results also showed that the analysis results of the coal by using these three methods did not differ significantly which can be seen from the resulting correlation coefficient namely above 0.99.

In addition, the comparison of the three methods of analysis showed that the methods of NAA and ICP-OES could generally be used for determining the concentration of the major elements to trace elements in coal samples comparing to the XRF method.

**Table 5.** Metal concentration in bottom ash using three methods

Elements	NAA		XRF		ICP-OES	Unit
Al	69300.00	± 60.00	NA		67100.00	mg.kg <sup>-1</sup>
Fe	130700.00	± 200.00	126300.00	± 4100.00	124600.00	mg.kg <sup>-1</sup>
Ti	4100.00	± 310.80	4000.00		4200.00	mg.kg <sup>-1</sup>
Ba	1300.00	± 27.60	1200.00	± 40.00	1200.00	mg.kg <sup>-1</sup>
Sr	417.34	± 55.78	406.6	± 36.53	400.00	mg.kg <sup>-1</sup>
Zn	NA		90.00		86.3	mg.kg <sup>-1</sup>
Cr	251.87	± 0.63	NA		226.02	mg.kg <sup>-1</sup>
Co	59.54	± 0.51	NA		60.58	mg.kg <sup>-1</sup>
La	185.58	± 0.11	175.95	± 3.72	189.23	mg.kg <sup>-1</sup>
Cd	12.32	± 0.65	NA		12.56	mg.kg <sup>-1</sup>

NA= not-analyzed

**Table 6.** Metal concentration in fly ash using three methods

Elements	NAA		XRF		ICP-OES	Unit
Al	83200.00	± 90.00	NA		88000.00	mg.kg <sup>-1</sup>
Fe	118600.00	± 200.00	114600.00	± 410.00	115500.00	mg.kg <sup>-1</sup>
Ti	4600.00	± 188.70	4600.00		4600.00	mg.kg <sup>-1</sup>
Ba	2500.00	± 68.40	3000.00	± 60.00	2900.00	mg.kg <sup>-1</sup>
Sr	730.51	± 41.91	713.09	± 43.23	700.00	mg.kg <sup>-1</sup>
Zn	189.92	± 22.36			178.68	mg.kg <sup>-1</sup>
Cr	142.71	± 1.24	NA		152.07	mg.kg <sup>-1</sup>
Co	61.43	± 0.56	NA		61.99	mg.kg <sup>-1</sup>
La	152.07	± 0.16	190.04	± 5.59	190.06	mg.kg <sup>-1</sup>
Cd	11.86	± 0.76	NA		12.18	mg.kg <sup>-1</sup>

NA = not-analyzed

Yet these two methods were an expensive method and NAA method requires a nuclear reactor and routine maintenance although this method could directly measure accurately in identifying the content in coal samples.

### Analysis of Bottom Ash and Fly Ash

Analysis of coal combustion products (bottom ash and fly ash) was performed by using three methods namely: NAA, XRF and ICP-OES.

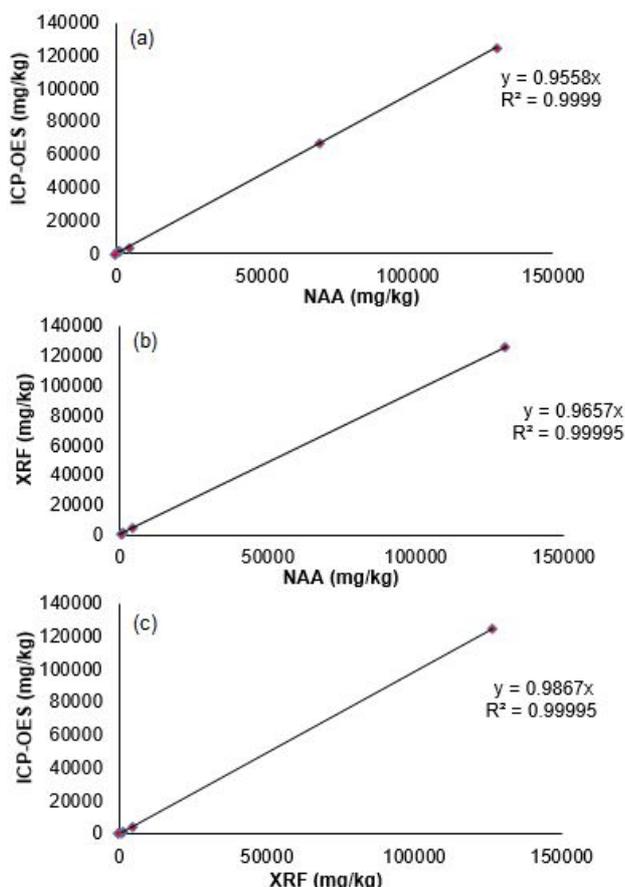
The analysis results of the major elements to trace elements in the samples of bottom ash and fly ash are detected some elements of major, minor and trace, have been 10 elements, namely Al, Fe, Ti, Ba, Sr, Zn, Cr, Co, La, and Cd will be discussed. The average concentration of the identified elements in the samples are shown in Tables 5 and 6. The total identified 10 elements was reported by Lim [8] were the elements that have a detrimental effect on humans, plants, and animals.

The analysis results in Table 5 and 6 showed that the relative abundance of the concentration of elements in the bottom ash found were Fe> Al> Ti> Ba> Sr> Cr> La> Zn> Co> Cd while on fly ash samples the elements concentration of Fe> Al> Ti> Ba > Sr> La> Zn> Cr> Co> Cd. In general, the chemical composition of the bottom was very similar to the fly ash. The concentration of Al and Fe in bottom ash and fly ash using all these three methods tend to be in large enough concentrations, which was expressed as a major element and to the

elements of Ti, Ba, Sr, Zn, Cr, Co, La, and Cd were in the lower concentrations expressed as a minor element and trace elements. The concentration of Al and Fe were within in the range of 6 and 12-13% at the bottom ash and fly ash ranged between 8 and 11%. Therefore, the both of bottom ash and fly ash samples could be used for cement material because they contained high alumina and iron [19].

The element concentrations of Fe using these three methods tend to be larger than that of the element of Al in the sample bottom ash and fly ash, and for elements of Al on fly ash higher than the bottom ash. This is in contrast to the results of research conducted by Tiwari et al. [6] in which the concentration of the element Al in the bottom ash and fly ash greater than the elements Fe, and Al elements found to be higher in the bottom ash compared with fly ash. This indicates that the element content in the combustion products (bottom ash and fly ash) from the power plant will have different characteristics from other power plants in addition to the type and origin of coal. Analysis results of metals in the bottom ash using NAA obtained metal concentrations of Al, Fe, Ba, Sr, and Cr is greater than the XRF method and ICP-OES. On the fly ash, the concentration of the elements Al, Ti, Cr, Co, La, and Cd using ICP-OES method is greater than in the two other methods that NAA and XRF.

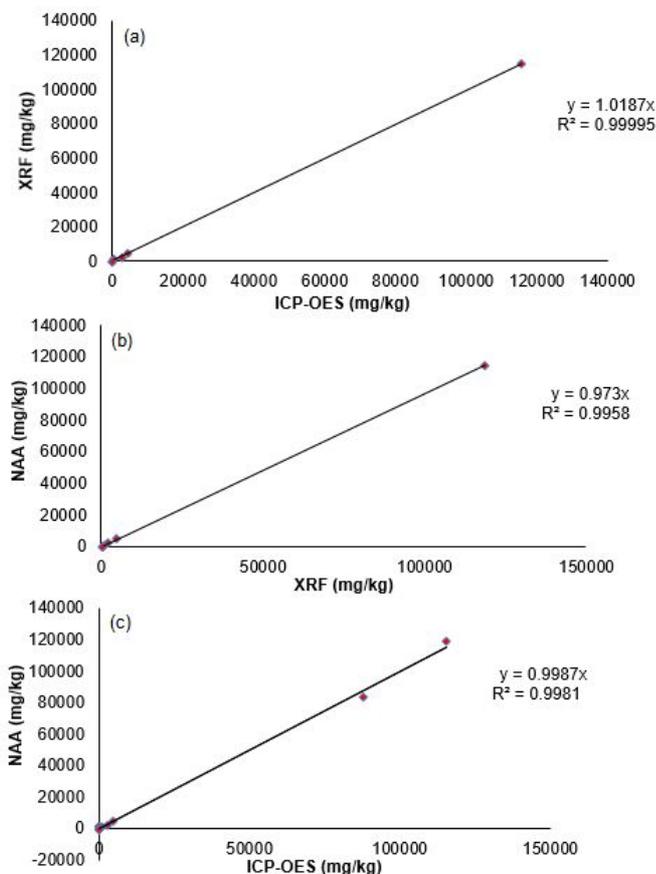
The use of the three methods in the analysis of heavy metals in bottom ash and fly ash intended as a complement if one method was not able to be good at



**Fig 2.** Comparison of concentrations of elements in samples of bottom ash obtained by using (a) ICP-OES vs NAA, (b) XRF vs NAA, (c) ICP-OES vs. XRF

giving analysis. Besides result, the use of various methods used to see how the correlation between these three methods to provide the results of the analysis element content in samples of bottom ash and fly ash Pacitan CPP. Correlation analysis results using NAA, XRF and ICP-OES were shown in Fig. 2 and 3.

The element concentration comparison in the samples of bottom ash in Fig. 2 shows that the comparison of the analysis results by using ICP-OES method vs NAA giving the slope = 0.9958 and correlation coefficient ( $R^2$ ) = 0.99920. Comparison between XRF vs NAA gave the slope = 0.9657 and  $R^2 = 0.99995$  while the results of the comparison between the ICP-OES vs. XRF gave the slope = 0.9867 and  $R^2 = 0.99995$ . Fig. 3 shows the results of elemental concentrations in fly ash by using XRF vs. ICP-OES gave the slope = 1.0187 and correlation coefficient ( $R^2$ ) = 0.99995. Comparison between NAA vs XRF gave the slope = 0.973 and  $R^2 = 0.99580$  while the results of the comparison between NAA vs ICP-OES gave the slope = 0.9987 and  $R^2 = 0.99810$ . Analysis result by using three methods could be concluded that various methods used

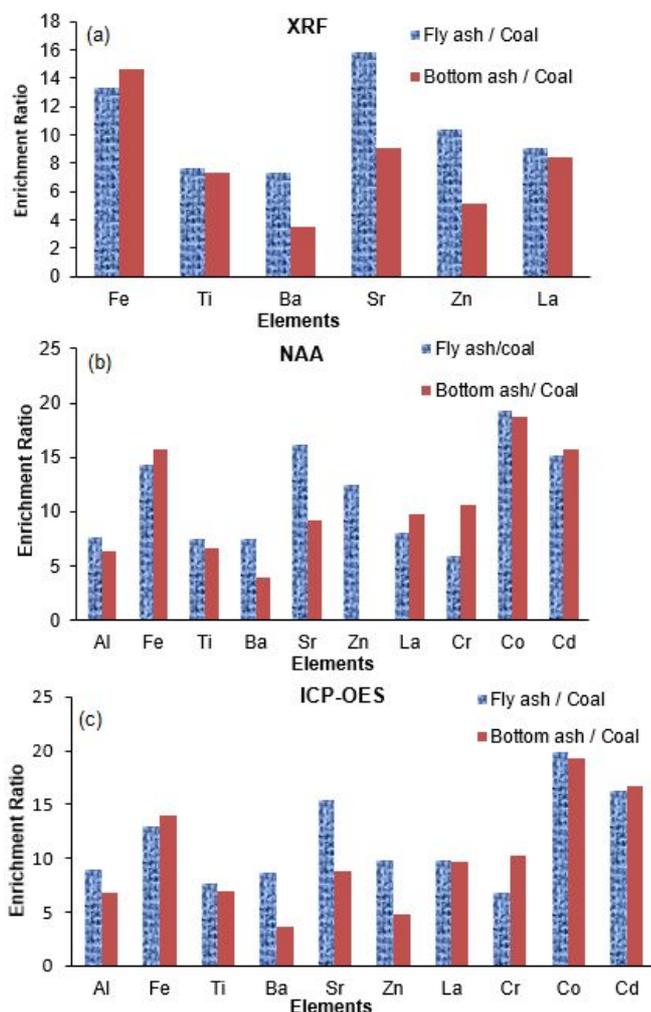


**Fig 3.** Comparison of the concentration of elements in fly ash samples obtained by (a) XRF vs. ICP-OES, (b) NAA vs XRF, (c) NAA vs. ICP-OES

in this research gave the good result one another in determining the element concentration in the fly ash and bottom ash.

Correlation of analysis results obtained by using the three methods was not much different from the results of research conducted by Damastuti [20] which stated that the correlation of analysis results for the concentration of elements in fly ash by using NAA, XRF and AAS methods yielded a good relationship with one another and did not differ significantly in providing analytical results. This is indicated by the correlation coefficient ( $R^2$ ) of the three methods, namely for the correlation between NAA vs XRF method yielded  $R^2 = 0.998$ , XRF vs. AAS method yielded  $R^2 = 0.99995$  and for the NAA and AAS method yielded  $R^2 = 0.982$ .

In general, the concentration of elements in the bottom ash and fly ash identified using three methods had not too much different except for La element. The comparison results also showed that these three methods have a good relationship in the determination of elements concentration in the samples. The concentration of Cr, Co, Cd, and Al elements in the



**Fig 4.** Enrichment Ratio (ER) for the elements in the bottom ash and fly ash compared to the elements in the coal using (a) XRF, (b) AAN, and (c) ICP-OES

samples of coal, bottom ash and fly ash could be identified by using the methods of NAA and ICP-OES but they could not be identified by using the XRF method. This is due to the limitation of XRF method, for low concentration of the Cr, Co and Cd elements below the detection limit, while for Al element was not detected because the atomic number <18.

The results of analysis by using three methods also showed that the concentration of Zn in the bottom ash can be identified by methods XRF and ICP-OES whereas with NAA method cannot be identified. This matter was due to Sc element in the spectrum has a wide peak so that Sc covers up the peak of Zn, where both elements of Zn and Sc having the characteristic gamma energy which is close enough namely Zn element was 1112 keV and Sc element was 1120.55 keV [21]. Allegedly, if the levels of the elements Sc quite large compared to Zn in samples of bottom ash

as research Murniasih with volcanic ash [21], the spectrum has a peak width Sc so as to cover the peak of Zn. At the time of the determination of net area of Zn element is unreadable net value of the area so that Zn in bottom ash with NAA method can only be identified qualitatively and cannot be determined quantitatively.

### Enrichment Ratio (ER)

Enrichment Ratio (ER) value was calculated as the ratio of the concentration of elements in the ash to the element concentration in the coal. The value of ER was calculated to determine the enrichment factor in the coal combustion waste associated with the used coal. Fig. 4 shows that ER for the elements in the bottom ash and fly ash were compared to the elements in coal. The elements tend to condense on fly ash as the result of decreasing the temperature resulted in the element enrichment in it. Fly ash was a finer fraction compared to that of the bottom ash which causes the larger surface area for the condensation process. The factors of ER from major, minor and trace elements have a high affinity for the smaller particles that ER of fly ash would be larger than the ER of bottom ash. Organic elements bonded are partly could evaporate and condense on the fine particles of fly ash which leads to higher concentrations in fly ash compared to the bottom ash [22].

The elements were analyzed using three methods showed that Al, Ti, Ba, Sr, Zn, and Co were found to be enriched in the fly ash compared with bottom ash except for the element La analyzed by NAA method further enriched in the bottom ash. The elements such as Fe, Cr, and Cd were analyzed using three methods were found to be enriched in the bottom ash. Among the elements analyzed, the maximum element enrichment observed in Co elements in fly ash and bottom ash.

Bhangare [23] stated that ER value below 1 indicates that the element was emitted together with off-gas because its volatile properties. Fig. 4 showed that as the whole ER value in the elements identified at the bottom ash and fly ash having the value >1. This matter identified that the properties of identified elements in general were non-volatile.

From Fig. 4 and also Fig. 1, 2, and 3 can it be seen that the method of ICP-EOS provides the most satisfactory analytical results. Seen from Fig. 4, there are four elements that are not detected by XRF method in all samples, one element is not detected by methods NAA in one sample (bottom ash), and 10 elements detected by ICP-EOS method in all samples. In Fig. 1, 2 and 3 it is shown the correlation coefficient  $R^2 = 0.99995$  and  $0.99996$  or close to 1. For further research, it is suggested to use ICP-EOS method for

the analysis of elements in the sample, because the result is already qualified, and if compared to NAA method, moreover ICP-EOS method uses cheaper tool and its maintenance, simpler in operating, needs fewer workers, and does not produce radioactive waste.

## CONCLUSION

Based on the data from the research and discussion, it could be concluded as follows: The analysis of multi elements simultaneously with NAA, ICP-OES and XRF methods showed that all of these three methods could generally be used for determining the concentration of an element of major, minor and trace elements in samples of coal, fly ash and bottom ash. Data of elemental analysis in the three samples, with three methods have an adjacent concentration value, which was shown by the value of  $R^2$  closes to 1. ICP OES method was most satisfactory in this study. The method of NAA is the most expensive method, because it requires a nuclear reactor and a lot of human resources that have specialized expertise. In addition, because of its accuracy and reliability, NAA is generally recognized as the "referee method" of choice when new procedures that are being developed or when other methods yield results that do not agree in XRF or ICP-OES. The data showed that the overall value of ER in the elements identified in bottom ash and fly ash has a value of greater than 1 (one). It indicates that the elements identified are generally non-volatile.

## ACKNOWLEDGEMENT

The author indebted to PSTA-BATAN who has allocated research funding of DIPA 2015. Sincerely thanks are also addressed to all the laboratory staffs of Nuclear Analysis Technique Division, for all your help so that this research could be completed.

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