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APPLICATION OF NUCLEAR ANALYTICAL TECHNIQUES IN CHARACTERIZATION OF SEVERAL SAMPLE MATRICES

APLIKASI TEKNIK ANALISIS NUKLIR DALAM KARAKTERISASI BERBAGAI MATRIKS SAMPEL

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ABSTRACT

The existence of elements in major, minor, and even in trace levels could have a significant impact on human health, environmental, industry, or other life sciences. Results of characterization from several matrices of samples could become as valuable and important information since a lot of important decisions regarding public health, environmental protection, and international trade is based on those results. Characterization of several matrices of samples requires excellence, reliable, and complies with ideal criteria as an analytical method. In recent years, nuclear analytical techniques become one of the analytical techniques that could meet the challenge of capability in characterization various matrices of samples and have been proven to be suitable and applicable in a broad range of applications. Nuclear analytical techniques deal with nuclear excitations, electron inner-shell excitations, nuclear reactions, and/or nuclear decay. These techniques are selective with high sensitivity, non-destructive, simultaneous, and limit detection microgram until nanogram level. In this paper, the role and contribution of nuclear analytical techniques used for BATAN research, especially neutron activation analysis (NAA), particle-induced X-ray emission (PIXE), and X-ray Fluorescence (XRF) in the characterization of various matrices of geological, pharmacy, biology and environmental samples were discussed. The comparison with other methods was also carried out. The validations of results were conducted by analysis of standard reference material (SRM). Discussion related optimization of parameter measurement and similar efforts were also presented. The results of this research are hopefully could show and emphasize the significant role of NAT in the characterization of several matrices of samples in contribution and support the life sciences and public welfare.

Keywords: Nuclear analytical techniques, NAA, PIXE, XRF, geological, environmental.

ABSTRAK

Eksistensi unsur-unsur yang berada dalam jumlah mayor, minor, dan bahkan dalam jumlah trace, dapat memiliki dampak signifikan dalam kesehatan manusia, lingkungan, industri, atau bidang kehidupan lainnya. Hasil karakterisasi dari beberapa matriks sampel dapat menjadi informasi yang berharga dan penting karena banyak keputusan penting mengenai kesehatan masyarakat, perlindungan lingkungan dan perdagangan internasional didasarkan pada hasil tersebut. Karakterisasi beberapa matriks sampel membutuhkan teknik yang unggul, dapat diandalkan, dan memenuhi kriteria ideal sebagai metode analisis. Dalam beberapa tahun terakhir, teknik analisis nuklir menjadi salah satu teknik analisis yang dapat memenuhi tantangan dalam kemampuan karakterisasi berbagai matriks sampel dan telah terbukti sesuai dan dapat diterapkan dalam berbagai aplikasi. Teknik analisis nuklir berhubungan dengan eksitasi nuklir, rangsangan kulit dalam elektron, reaksi nuklir, dan/atau peluruhan nuklir. Teknik-teknik ini selektif dengan sensitivitas tinggi, non-destruktif, simultan, dan limit deteksi mikrogram hingga tingkat nanogram. Dalam makalah ini, dibahas peran dan kontribusi teknik analisis nuklir yang digunakan untuk penelitian BATAN terutama Neutron Activation Analysis (NAA), Particle Induced X-Ray Emission (PIXE) dan X-Ray Fluorescence (XRF) dalam karakterisasi berbagai matriks geologi, sampel farmasi, biologi dan lingkungan. Perbandingan dengan metode lain juga dilakukan. Validasi dilakukan dengan analisis bahan acuan standar Standard Reference Material (SRM). Diskusi terkait optimasi pengukuran parameter dan upaya terkait juga

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disajikan. Hasil penelitian ini diharapkan dapat menunjukkan dan menekankan peran signifikan teknik analisis nuklir (TAN) dalam karakterisasi beberapa matriks sampel dalam kontribusi dan mendukung ilmu kehidupan dan kesejahteraan masyarakat.

***Kata kunci**: Teknik analisik nuklir, AAN, PIXE, XRF, geologi, lingkungan.*

I. INTRODUCTION

Research related to the analysis and development of the capability in the characterization of various elements accurately and validly is needed to support various government programs such as food security, advanced materials, nutrition, environment, health, and medicine programs [1–13]. Various problems related to the need for information on the composition characteristics of multiple elements in the sample demanded comprehensive research in the development of analytical methods and application of analytical techniques for identification. This characterization step is a start in the study and development of further research in the fields of industry, agriculture, mining, advanced materials, food, health, and the environment, which need supporting tools in optimizing related research [1–13]. Various sample matrices such as food, health (such as medicines, organs, human body tissue, serum, hair, and so on), environment (such as soil, air, water, sediment), geology, industry, materials, and other samples generally contain various kinds of elements both major, minor and trace [4,6–8,14].

The existence of an element, even at very low levels of trace, can have a very significant impact on human health, the environment, or industry. In biomedical science, it is known that there is a correlation between deficiency or excess of certain elements with symptoms of health problems]15–17]. Lack of micronutrients in food as the body's intake also impacts its function as a metalloenzyme in the process of biochemical reactions and metabolic systems [18,19]. In the field of environment, the elements contained in environmental samples generally can provide an overview of the level of toxicity and quality of the environment and can be used as a key element in identifying sources of pollutants [3,20]. The element concentration assessment in the environmental sample matrix can be used to review compliance with environmental regulations or quality standards (generally below 10-10 g/g) [21]. The concentration of an element in the environment can also be an early warning of the level of exposure received by the community. Therefore it can be used as a scientific-based foundation in making appropriate and directed policies in an effort to improve environmental quality, health problems, and greater financial losses can be avoided. In the industrial sector, identification of elements as impurities (generally at the level of 10-12 g/g) in an industrial product, especially advanced materials, is needed in determining the quality, designation, and selling price of these. Of these various needs, comprehensive research in developing analytical methods and application of analytical techniques for the identification of elements in various sample matrices is needed.

In the 19th century, when various analytical methods for characterization of samples were developed, many elements in various sample matrices were not detected, especially elements at the minor and trace levels. Along with technological advances and characterization capabilities, trace elements and even ultra-trace can be detected properly. BATAN is expected to

contribute significantly to solving national problems by prioritizing the application and implementation of nuclear-based technology. The nuclear analytical technique is one of the analytical techniques that have the prospect of increasing characterization capabilities on various sample matrices. The nuclear analytical technique (NAT) is an accurate, sensitive, non-destructive, multi-elemental analysis technique capable of detecting in micro order to nanogram [22,23]. In this context, BATAN Bandung, through research activities related to the application of nuclear analysis techniques, has carried out various applications that prioritize the advantages of nuclear analysis techniques as a solution to overcome the limitations of conventional analytical techniques and promote independence in the analysis.

NAT nuclear analytical technique is defined as an analytical technique related to the principles of core excitation, electron excitation, nuclear reactions, and/or radioactive decay. NAT can include analytical techniques such as Neutron Activation Analysis (NAA), ion beam analysis - Particles Induced X-ray Emission (PIXE), and X-Ray Fluorescence (XRF) (21–23). These techniques are a very selective elemental analysis technique with high sensitivity, non-destructive, simultaneous, and has a limit of detection reaching the order of micrograms and even nanograms. One of the capabilities shown by the PIXE technique is characterization using this technique can analyze the number of samples up to hundreds of samples per day and only requires a small sample weight of ~ 100 µg. This reason makes nuclear technique as an analysis technique that is worth considering for the analysis of various sample matrices compared to conventional analysis techniques. Cahill, 1990 stated that almost 90% of air particulate filter samples in North America were analyzed using nuclear techniques. Even in Australia in the last four years, more than 9000 filter samples have been analyzed using nuclear techniques, specifically PIXE [24].

This paper aims to introduce the application of nuclear analytical techniques, especially NAA, PIXE, and XRF, on the characterization of various sample matrices by optimizing various parameters. It includes quality assurance of test results in the form of validation methods using a variety of standard reference materials (SRM) or comparison with other methods to show that NAT has the superior and reliable ability in characterizing various sample matrices.

II. METHODS

1. Neutron Activation Analysis

Neutron activation analysis (NAA) is an analytical method for the qualitative and quantitative determination of elements based on the measurement of the gamma-ray radiation characteristic of radionuclides that are formed directly or indirectly through the process of neutron irradiation on a material. The elemental concentrations are calculated by the comparative method [23]. Samples are irradiated with neutrons in reactors or accelerators. Nuclides that are stable in the sample (the target of the nucleus) will experience a neutron capture reaction, thus forming a radioactive nucleus (compound nucleus). In general, these radioactive nuclides will undergo decay through beta and gamma emission. After the sample is taken out from the reactor, the sample will emit radiation as a radioactive decay process. High-resolution spectrometers are used to detect delayed gamma rays. The irradiation of the sample depends on the neutron flux and the half-life of the radionuclides to be analyzed [25,26]. The detailed related NAA and the experimental preparation, as well as the quantitative and qualitative analysis, were described else [23]. Table 1 showed the list of radionuclides that generally detected in NAA.

2. Neutron Activation Analysis

PIXE is one analysis technique that utilizes an ion beam (ion beam analysis - IBA). This technique has a basic working principle in the form of interaction between accelerated particles (particle beam) with the material. Charged particles that are accelerated using an accelerator, when interacting with the material, will interact with electrons and atomic nuclei, exciting electrons from the deepest atomic shell. Electron excitation (generally K or L shells) will cause electron expelled, and the configuration becomes instability so that electrons from the outer shell will move to fill this hole, which will release excess energy when displaced in the form of X-rays [27]. This X-ray energy is characteristic for each element, so it can be used to identify certain elements contained in the material or material being analyzed [24,27,28]. The area of the peak of the X-ray in the spectrum produced is proportional to the number of atoms contained in the sample. This is used to determine the concentration of an element through comparison with known standards. The detailed of experimental preparation and measurement is written elsewhere [24,27,28].

3. X-Ray Fluorescence

The principle of measurement using XRF is the same as the principle in PIXE. It is based on the event of electron excitation when an atom in an element is bombarded or interacts with X-rays. Following the Pauli principle, the electron-hole will then be filled by electrons coming from outside orbitals and, at the same time, will always be accompanied by the release of X-rays that are characteristic for each element [29,30]. In qualitative analysis, XRF method can identify elements from the atomic number (Z) = 4, namely Be to Z = 92 (U) and has a measurement range from µg/g to %, and the detection limit at the level of µg/g without preconcentration. Although Inductively Couple Plasma (ICP), Atomic Absorption Spectrophotometry (AAS), Neutron

Table 1. List of radionuclides that can be detected well by NAA[23,25,26]

Element	Nuclide	Half life	Energy (keV)
Al	^{28}Al	2.24 m	1778.9
As	^{76}As	26.3 h	559.1
Ca	^{49}Ca	8.7 m	3084.4
Ce	^{141}Ce	32.5 d	145.4
Co	^{60}Co	5.27 y	1173.2; 1332.4
Cr	^{51}Cr	27.72 d	320
Cs	^{134}Cs	2.06 y	795.8
Fe	^{59}Fe	44.5 d	1099.2
Hf	^{181}Hf	42.4 d	482.2
Hg	^{203}Hg	46.6 d	279.2
K	^{42}K	12.36 h	1524.7
La	^{140}La	40.23 h	1596.2
Mg	^{27}Mg	9.45 m	843.7; 1014.4
Mn	^{56}Mn	2.58 h	846.7; 1810.7
Na	^{24}Na	15.02 h	1368.6; 2754.1
Sb	^{124}Sb	60.2 d	1691
Se	^{75}Se	119.8 d	264.7; 279.5
Sm	^{153}Sm	46.7 h	103.2
Sc	^{46}Sc	83,8 d	889,3; 1120,5
Th	^{233}Pa	27 d	311,9
Ti	^{51}Ti	5,8 m	320,1
U	^{239}Np	23,5 d	74,7; 277,7
V	^{52}V	3,76 m	1434,1
Zn	^{65}Zn	243,8 d	1115,5

m/minute; h/hour, d/day, y/year

Activation Analysis (NAA) and various mass spectrometry have much lower detection limits, the broad range of measurement is a unique characteristic of XRF. This XRF method can measure Pb, Cd, and S which cannot/are difficult to determine with NAA. If the two methods (NAA and XRF) are combined, it will produce extraordinary characterization capabilities.

These nuclear analytical techniques that will be applied in characterizing various sample matrices have various advantages and limitations. A comparative resume of these three methods with other methods is summarized in Table 2.

4. Geological samples (zircon sand and iron sand)

Zircon sand is a natural material that contains natural radioactive elements; this sand is suspected of having uranium and thorium content, which is quite large (in the order of ppm) if it is mined in a certain amount. Likewise, iron sand, which is suspected of having a quite large amount of U and Th. Therefore, it is necessary to know the concentration of uranium and thorium in the sand quantitatively. Besides that, the elements of Al, Fe, Ti, Na, Zr, and Hf are also determined. Zircon sand and iron sand that have been dried and homogenized were taken 25 mg each, then put into polyethylene vials for short irradiation, medium irradiation, and long irradiation [32]. The sand samples in the vial are then ready to be irradiated by neutrons in the Siwabessy Multipurpose Reactor (RSG), Serpong. For measurement of Al and Ti concentrations, samples were irradiated for 1 minute; for measurements of elements with medium half-life such as elements U and Na samples are irradiated for 15 minutes; while for measurement of Th and other elements of long half-life (Hf, Zr, etc.) samples are irradiated for 2 hours. Neutron irradiation of the zircon sand sample causes ^{238}U and ^{232}Th nuclides contained in the sample to be activated into new radionuclides with the following reaction equation:

$$^{238}U + n \rightarrow ^{239}U \rightarrow ^{239}Np$$

$$^{232}Th + n \rightarrow ^{233}Th \rightarrow ^{233}Pa$$

U and Th measurements are carried out using Np and Pa respectively, because after some time cooling U and Th decays into Np and Pa respectively [33].

5. Pharmaceutical samples (supplements)

In this study, elemental analysis was carried out on a supplement sample, spirulina, which is widely used as an additional source

Table 2. Comparison of nuclear analytical techniques and others [21,22,24,31]

	NAA	PIXE	XRF	ICP/MS/ AES	AAS
Multi-elemental	Yes	Yes	Yes	Yes	No
Sensitivity	Good	Fair	Fair	Good	Good
Accuracy	Very Good	Fair	Fair	Good	Good
Limit detection	0.001-30 ng/m^3	1-12 ng/m^3	0.5 - 5 ng/m^3	0.02-60 ng/m^3	0.001-40 ng/m^3
Time of analysis	Quite long	Fast	Fast	Medium	Medium
Matrices effect	Little	Yes	Yes	Little	Rare
Sample preparation	Simple	Very simple	Very simple	Digestion	Digestion
Cost	High	High	Medium	Medium – High	Medium
Limitation	Reactor access	Accelerator access Not accurate for light element (Na, Mg)	Not accurate for light element (Na, Mg) Standard	Maintenance, standard and gas	Cathode lamp

of vitamins. Spirulina is a kind of aquatic algae that is bluish green. Spirulina is one of the platensis species; it is safe to consume and has high nutritional value, including Fe and Zn, which are needed in the physiological processes of living things to help enzymes work and organ formation. In this paper, the discussion will be focused on the elements of Fe and Zn nutrition. Spirulina platensis samples were food supplement products that were ready for consumption under different trademarks. Samples were mashed to ~ 200 mesh size using mortar agate, then weighed as much as 25 mg, put into a 0.273 mL polyethylene vial, then sealed to close it. The sample is ready to be irradiated. The same thing was done on SRM NIST 1567a Wheat Flour. A standard solution of Fe, Zn, and Hg drops was prepared, weighing 40, 1, and 0.1 µg of Merck and $HgCH_3COO$ titrisol solutions, respectively. Samples and synthetic standards are ready to be irradiated for 2 hours at the GA reactor Siwabessy, Serpong [34].

6. Biological samples (human scalp hair)

In this study, the determination of sample elements using NAA techniques focused on the application of NAA analysis techniques on hair samples to obtain data on the normal concentration of trace elements in a population. In order to ensure the validity of the data, a similar analysis procedure is applied in analyzing the IAEA Human Hair 086 standard material-SRM human hair. Hair sampling is carried out according to the procedure recommended by the IAEA [35]. Hair samples and standard hair material IAEA 086 each weighed as much as 50 mg, put in a polyethylene vial measuring 0.273 mL, then sealed by heat. Samples, along with the standard irradiated G.A Siwabessy reactor Serpong was then counted using a gamma ray spectrometer for 10,000 seconds, after cooling it for several weeks. Gamma spectrum analysis and interpretation were performed using Genie-2000 software. With this condition, several results are focused on the toxic elements of Co, Cr, and Hg [36].

7. Geological samples (zircon sand and iron sand)

For measuring coal fly ash samples, besides NAA method, the Minipal4 EDXRF was used. This EDXRF was equipped with a Rh tube as an x-ray generator (9 W X-ray tube, Max 30 KV, max 1 mA), 5 filter tubes, silicon detector, and 12 sample trays position with sample spinner. The sample spinner system provides constant rotation during measurement to reduce errors due to homogeneity in sample preparation [37,38]. Characterization of samples using XRF was carried out using the Minipal4 for powder/ solid samples such as coal fly ash samples, and Epsilon5 for air particulate samples. In characterizing the sample using XRF, the parameters that need to be optimized are standard calibrations, secondary targets, measurement conditions, currents, voltages, and measurement times. Changes in these parameters will greatly affect the optimization of the results obtained. Preparation for measurements using XRF does not take much time and special treatment. For powder samples, the sample is dried, homogenized through grinding and sieving, then ready to be placed into the sample holder. For air particulate filter samples, just place them in the sample holder and measurement tray. The optimum condition for this measurement has been optimized, and validation also applied.

III. RESULTS AND DISCUSSION

1. Geological samples (zircon sand and iron sand)

Uranium (U) and Thorium (Th) measurements were carried out on 26 zircon sand samples in the Kalimantan area and iron sand from Java. The energy used in uranium counting is energy from Np that is 103.18; 228.2 and 277.7 keV, while for thorium, Pa is used at 312 keV energy [33]. The results of the method validation

using the National Institute of Science and Technology SRM - NIST Montana Soil 2711a are summarized in Table 3. Validation showed good recovery and precision. The results of U and Th analysis on zircon sand from Kalimantan are shown in Figure 1. The results of U and Th analysis on zircon sand samples indicated that the range of uranium is in the range of 28.6 to 500.8 mg/kg, while for thorium ranges from 19.7 to 612.1 mg/kg [32]. Most of the sand has U and Th content above 100 ppm, which is the reference limit of safety guidelines issued by the IAEA, which states that an industrial activity that produces radioactive nature must be taken if the uranium or thorium content is more than 100 ppm [39]. Potential as a source of uranium and thorium in zircon sand must get special handling of regulations regarding the export of zircon sand abroad. The results of this analysis can be a reference in drafting regulations related to zircon sand mining or trading. Meanwhile, zircon content in the sand is in the range of 1.1-31.8%.

The results of U and Th concentrations on iron sand from West Java and East Java are shown in Figure 2. Uranium content in iron sand is in the range of 0.2-5.2 mg/kg with a mean value of 2.1 ± 1.3 mg/kg, while thorium levels are in the range of 0.3-3.6 mg/kg with an average of 1.9 ± 0.8 mg/kg [40]. Uranium and thorium levels in iron sand are also included as normal levels in the sand and are still below the 100 mg/kg limit. When compared with the results of measurements of uranium and thorium levels in sand samples in several countries also provide values that are not much

Table 3. Results of IAEA RM Soil-7 and NIST 2711a [32]**.**

Element	Analysis result (mg/kg)	Certificate value (mg/kg)	Bias (%)
IAEA RM Soil-7			
Th	15	15	0.0
NIST 2711a			
Th	8.18	8.2	-0.2
U	3.07	3.01	2.0

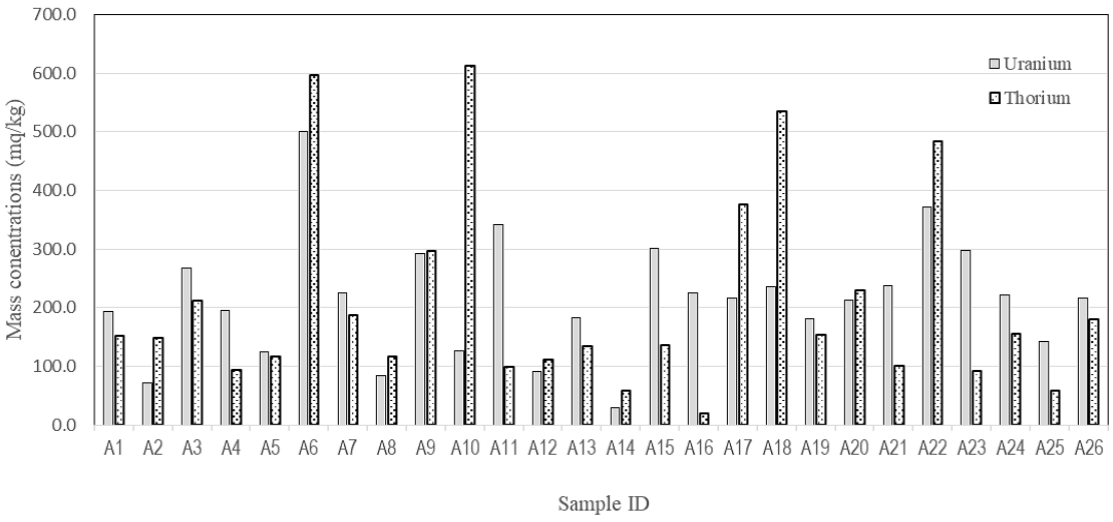

Figure 1. Mass concentration of U and Th in zircon sands [32]**.**

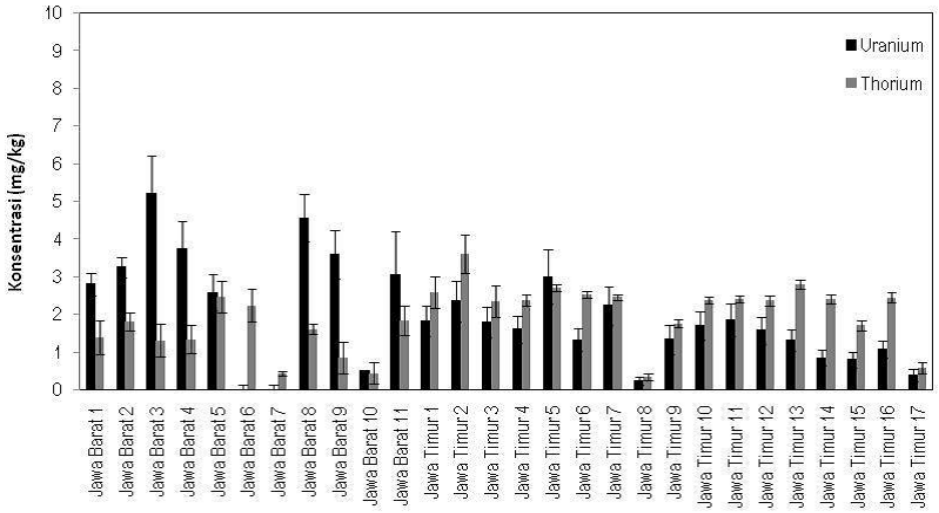

Figure 2. Concentrations of U and Th iron sand samples in West Java and East Java [40]**.**

different. Iron content in iron sand samples ranged from 5.4 to 49.5%, which shows that there were several iron sands that have high grades. Through the characterization of iron sand samples, this potential can be further optimized.

2. Pharmaceutical samples (supplements)

The results of the characterization of spirulina supplement samples using NAA for Fe and Zn are shown in Table 4. Method validation was carried out by SRM Wheat Flour 1568a analysis. The analysis of Fe and Zn elements in SRM samples gives a recovery of 99 and 101%, respectively [34]. From Table 4, the Fe content of the three spirulina platensis products was varied 647.3; 693.3 and 3320.8 mg/kg, while the Zn content was 19.2; 26.4 and 43.3 mg/kg. The content of Fe and Zn in the first and second product samples is in the normal range for Fe and Zn in general commercial spirulina products ranging from 300-1000 mg/kg and 20-35 mg/kg [34]. Whereas in the third sample for the NAA Fe element (3321 mg/kg) showed significantly different results and was greater than the other two samples both by the NAA and AAS methods. The results of the sample analysis show a good fit between the NAA and AAS methods, as indicated by the linear regression values for Fe and Zn, respectively 0.9999 and 0.9860, respectively. This showed the suitability between the NAA and AAS methods so that they can overcome the limitations/weaknesses of the two methods and can complement each other for analysis [34].

3. Biological samples (human scalp hair)

The application of NAA techniques to biological samples is carried out on

Table 4. Fe and Zn results of suplement samples spirulina plantesis [34]**.**

No.	Samples	Fe (mg/kg)		Zn (mg/kg)	
		NAA	AAS	NAA	AAS
1.	Spirulina 1	647.3±8.0	682±5.5	19.2±1.0	18.9±1.3
2.	Spirulina 2	693.3±7.5	730±13.5	26.4±0.7	29.4±1.2
3.	Spirulina 3	3320.8±18.3	3256±18.7	43.3±1.1	44.9±2.3

Table 5. Analysis results of CRM GBW 76101 dan NIES 13 [36,42]**.**

Sample	Element	Analysis results (mg/kg)	Certificate value (mg/kg)	% *recovery*
GBW 76101	Co	0.070±0.05	0.071±0.01	98
	Cr	0.37±0,06	0.37±0,06	99
	Hg	0.37±0.08	0.36±0.08	101
NIES 13	Cr	4.6±0.06	4.77±0.06	96

Table 6. Results of several heavy metals in human hair [36,42].

Element	Traffic service officer	Control	Ratio
	Average (mg/kg)		
Co (n=35)	0.065±0,01	0.058	1.10
Cr (n=32)	0.27±0.13	0.87	3.36
Hg (n=32)	1.41±0.10	4.72	3.23

the characterization of hair samples. This study aimed to determine the impact of occupational exposure to health problems through hair biomarkers of employees of the transportation industry in Bandung. The focus of the activity was the content of toxic elements such as Co, Cr, and Hg in the hair samples of the employee [36]. Method validation is done by analyzing the human hair CRM GBW76101 and NIES No. 13. The results of the validation are shown in Table 5. The results of the elemental analysis on the two standard reference materials show good compatibility with the value of the certificate value with %recovery in the acceptable range under 10% [36]. This value is within the acceptable range, where for elements in the range of ~ 10 ppm, it is within the limit of 80-115% recovery [41]. The average and concentration range of the elemental analysis results in hair and control samples are shown in Table 6.

Determination of Hg with NAA was applied using gamma energy at 279.6 keV, but at this energy, there is overlapping with Se at 279.2 keV. To overcome it, corrections were made using Se normalization at 400.7 keV [26]. Whereas for Co and Cr, there were no interferences on the spectrum. From the results, the concentration of Cr, and Hg elements in the hair of transportation industry employees have a higher tendency than in control hair. The high Cr in the hair of employees in the transportation industry is compared with controls in accordance with the results of the study of Ramakhrisna et al. [43].

4. Environmental samples (coal fly ash and airborne particulate matter)

4.1. Coal fly ash

Characterization of environmental samples using NAA was applied to coal fly ash samples. Quality control in the form of SRM sample testing with the same matrix is performed on NIST 1633b coal fly ash SRM samples. The results of the SRM analysis are summarized in Table 7. Figure 3 showed the quality control of coal fly ash analysis.

Comparison analysis of coal fly ash samples with NAA and XRF was resumed in Table 8. It can be seen that there is a good agreement between the NAA and XRF results.

4.2. Airborne particulate matter

The results of the characterization of air particulate samples obtained from the Bandung area are summarized, as shown

Table 7. Analysis results of SRM NIST 1633b coal fly ash [44]**.**

Element	Certificate value (mg/kg)	Analysis results (mg/kg)	Bias (%)
Al*	15,05 ± 0,27	15,52 ± 0,73	3,1
As	136,2 ± 2,6	135,7 ± 2,3	0,4
Ce	190	182 ± 10,2	4,2
Co	50	51,3 ± 3	2,6
Cr	198,2 ± 4,7	192,3 ± 9,4	3,0
Fe*	7,78 ± 0,23	7,74 ± 0,23	0,5
K*	1,950 ± 0,030	1,980 ± 0,037	1,5
La	94	88,4 ± 3,1	6,0
Mn	131,8 ± 1,7	131 ± 6,0	0,6
Na*	0,201 ± 0,003	0,221 ± 0,003	9,5
Sc	41	40,8 ± 0,6	0,5
Sm	20	19,0 ± 0,1	5,0
Ti*	0,791 ± 0,014	0,788 ± 0,118	0,4
V	295,7 ± 3,6	283,6 ± 28,1	4,1

Note: * in percent

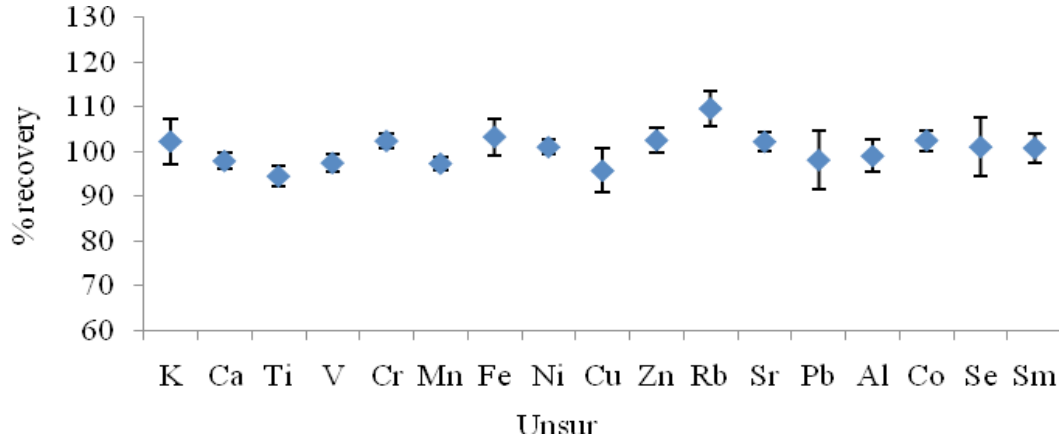

Figure 3. The accuracy of the results of the SRM 1633b Coal Fly Ash analysis using the XRF method [44].

Table 8. Comparison results of NAA and XRF in coal fly ash samples [44]**.**

Element	**NAA**	**XRF**
Al (%)	11,7 ± 5,1	12,2 ± 0,91
Fe (%)	9,02 ± 0,29	8,99 ± 0,12
Ca (%)	3,96 ± 0,37	3,79 ± 0,04
Ti (%)	0,52 ± 0,08	0,48 ± 0,014
K (%)	0,65 ± 0,08	0,65 ± 0,038
Co (mg/kg)	60,3 ± 3,6	62,7 ± 6,9
Cr (mg/kg)	112 ± 9,3	126 ± 10
V (mg/kg)	117 ± 6	113 ± 7
Zn (mg/kg)	256 ± 19	254 ± 3

in Figure 4. From all elements detected in the $PM_{2.5}$ sample (particulate matter with an aerodynamic diameter less than 2.5 µm), it is shown that the elements Na, Cl, Al, Si, S, K, Ca, and Fe are the elements with the dominant concentration in the samples. Other trace elements such as V, Cr, Cu, Ni, Hg, and Pb can be detected properly using

PIXE. These elements play a sufficient role that can indicate sources of anthropogenic pollution such as industries, chimneys, or certain metal industries.

Comparison of the PIXE and NAA methods was also carried out on the same sample, where a ratio of 0.97 ± 0.01 with a coefficient of R2 = 0.99 was obtained (Figure 5) [24]. This result shows a very good suitability even if the analysis is done in a different laboratory. Several other studies also confirm that PIXE gave very significant results in the analysis of air particulate samples [1,20,28].

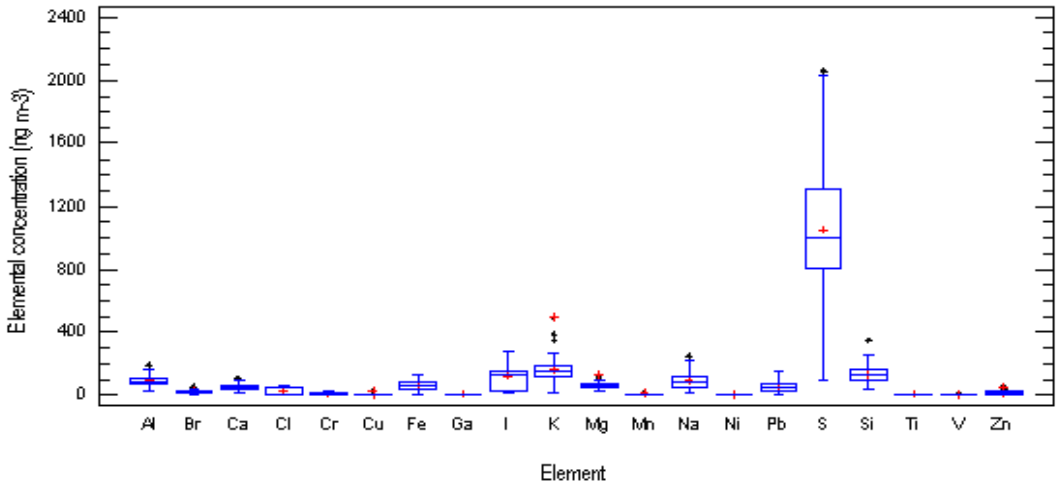

Figure 4. ***Whisker plot*** **of several elements in the APM by PIXE** [45]

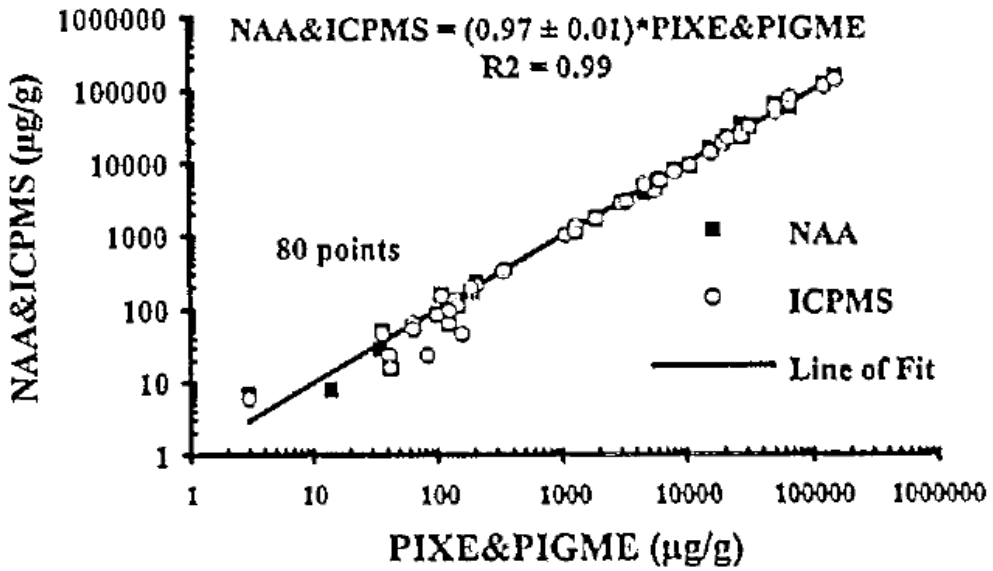

Figure 5. Comparison NAA, ICPMS and PIXE-PIGME [24]

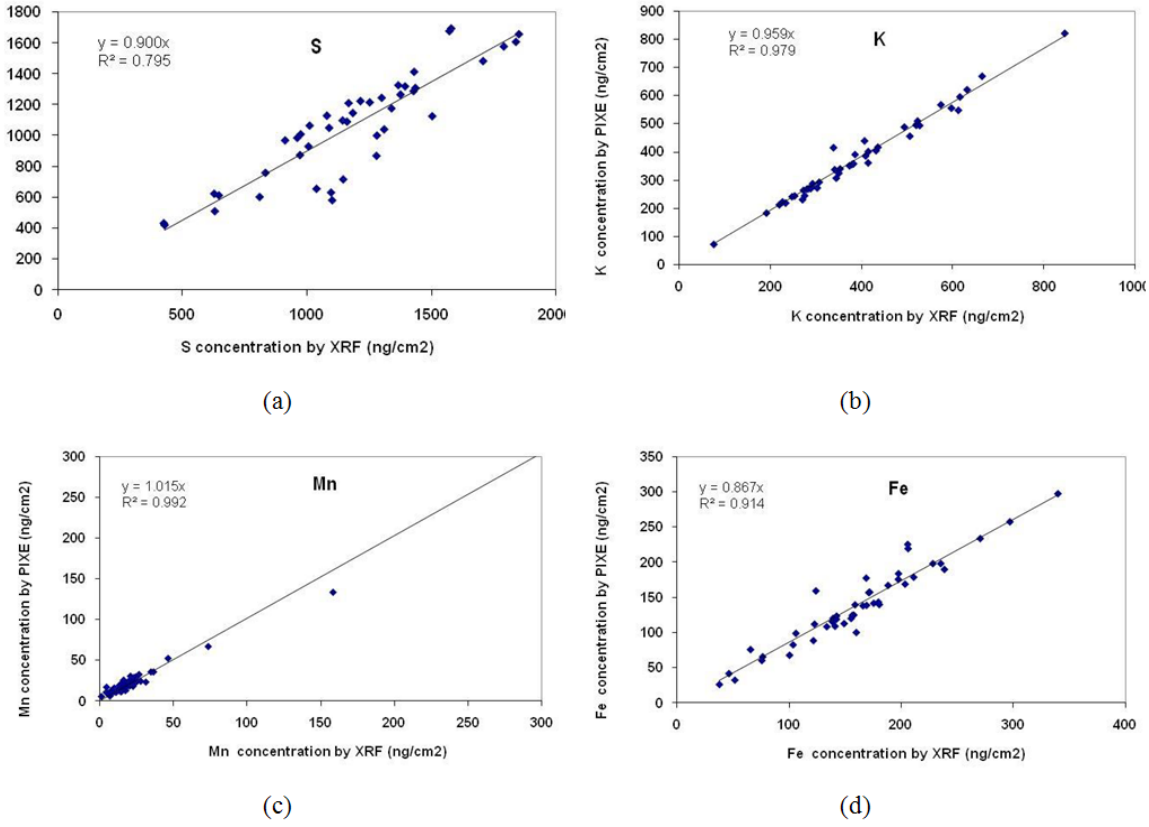

Figure 6. Comparison of results on S, K, Mn and Fe by XRF and PIXE [46]

To guarantee the results of the XRF test, the results were compared with PIXE. Comparative results for several elements are shown in Figure 6. PIXE measurements were carried out at Geological Nuclear Science, New Zealand. It can be seen that for the elements S, K, Fe, and Mn there is a good match between the XRF and PIXE techniques.

IV. CONCLUSION

The application of NATs in particularly NAA, PIXE, and XRF on various samples, validation, and comparison with other methods, showed that NAT is an analytical technique that has good and reliable accuracy and precision in the characterization of the various sample matrix. This capability is good in terms of excellence, multi-element, good detection limits, which will be the answer to the challenges of the need for characterization of samples in various fields. The data obtained is needed in the first step of each related research to be followed by further research in the form of interpretation, study, and policy-making and appropriate strategy in overcoming the existing problems. The end-users who need and utilize this characterization capability are not only the government but academics from various universities, researchers from private institutions, industrial, regional R&D institutions, and many others. The development of NAT, especially for PIXE, which is still not available yet in Indonesia, is encouraged and promising to be utilized in several fields of research.

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