ELEMENTS CHARACTERIZATION IN RICE FLOUR AND FISH MEAL FOR LABORATORY COMPETENCY

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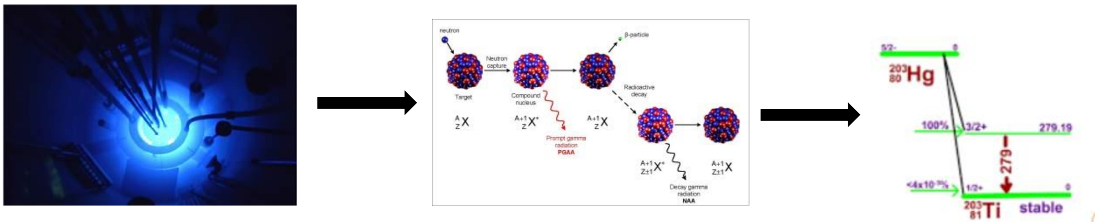
Abstract *Nowadays, nutrition problem becomes an important issue in many developing countries. Lack or excess macro and micro elements in food can interfere human health. Therefore, food safety needs a reliable analytical method in accuracy and precision. In this activity, characterization of toxic (As, Pb, Cd, Hg) and essential elements (Na, K, Ca, Mg, Fe,Cu, Zn) in rice flour and fish meal had been done using Neutron Activation Analysis (NAA) and Atomic Absorption Spectrophotometry (AAS). Both samples provided by The Asia Pacific Food Analysis Network (APFAN) on 2017. Three replications were prepared. Reducing the probability of contaminating the sample is a must. AAS needs homogenous liquid samples therefore samples were digested using microwave digestion to avoid loss of volatile elements from the samples. Evaluation on rice flour and fish meal samples analysis were based on Z-score value with 3 categories: satisfactory, questionable and unsatisfactory result. Both methods had satisfactory result in rice flour where Z-score value of K, Ca, Zn < 2 meanwhile AAS gave Mg, Fe, Cu, Cd < 2 in the same sample. NAA gave the Z-score 2 < Mg < 3 in rice flour. Satisfied performance in fish meal gave Z-score values of K, Ca, Mg, Fe, Zn < 2 for both of them. Values of Na < 2 and 2 < Hg < 3 obtained from NAA in fish meal and Z-score of As was < 2 with NAA. Moreover, 2 < Pb < 3 obtained from AAS in fish meal sample. These results showed that NAA and AAS are accurate and precise methods on food analysis in rice flour and fish meal from APFAN to maintain laboratory competency.*

INTRODUCTION

In this globalization era, laboratory competency to present a valid data result in elemental characterization is needed. This competency, is not only needed by free markets but also for analytical method services. Radiometric Analysis Technique Laboratory (TAR) applies Neutron Activation Analysis (NAA) and Atomic Absorption Spectroscopy (AAS) methods to answer the need of essential and heavy metals characterization in food.

Neutron Activation Analysis (NAA) is a method of qualitative and quantitative elements analysis. This method is based on convertion of stable atomic nuclei into radioactive nuclei by irradiation using neutrons and subsequent detection of the radiation emitted by the radioactive nuclei (1). Figure 1 showed basic principle of NAA



Neutron source (nuclear research reactor) (1)

Neutron capture (1)

^{203}Hg decay scheme (2)

Figure 1. Free surface boundary condition.

Radioactive element identification is obtained by detecting the characteristic γ rays produced using a set of γ spectrometers unit. The most common reaction occuring in NAA is the (n, γ) reaction as formula below:

$${}^{A}_{Z}X + {}^{1}_{0}n \rightarrow \left[{}^{A+1}_{Z}X\right] + {}^{0}_{0}\gamma \qquad (1)$$

with:
A = mass number of element;
Z = atomic number of element.

NAA is one laboratory which using nuclear research reactor facilities (3). In this activity, the characterization of elements in rice flour and fish meal were carried out at Bandung Triga 2000 nuclear research reactor. The advantages of NAA are could analyze elements simultaneously, specific, could measures elements up to ppb unit, simple in sample preparation and requires only a small number of samples. This method has been used widely in various fields such as in health, industry and environment (4-7).

In addition to NAA, elements characterization in rice flour and fish meal were also carried out using Atomic Absorption Spectrophotometry (AAS) as a complimentary and comparison method. This technique is based on absorption of radiation sources by free atoms in the sample. Figure 2 explains AAS stages method up to exitation process. There are many applications of atomic absorption spectroscopy (AAS) due to its specificity. These can be divided into broad categories of biological, environmental, marine and geological analysis (8-10). The advantages of this method are accurate, precise, specific and elements concentration range up to ppb (µg/L) unit.

Competency of a laboratory testing determines validity of the results could be done by participating in a proficiency test program. In this activity, TAR laboratory characterized elements in rice flour and fish meal provided by The Asia Pacific Food Analysis Network (APFAN) on 2017. The results obtained can be used as quality assurance because both methods have good accuracy and precision for characterization of essential elements and heavy metals in rice flour and fish meal and to maintain laboratory competency as well.

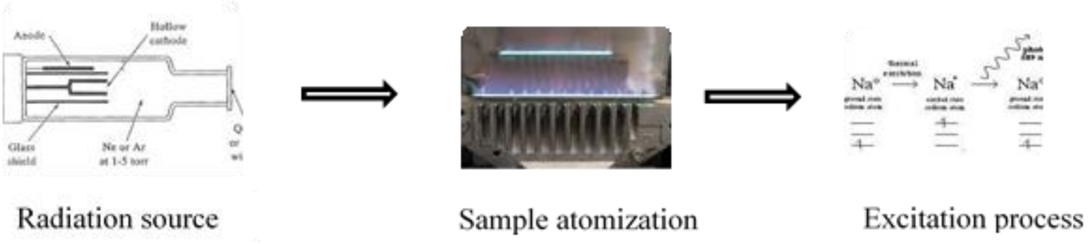


Figure 2. AAS excitation process (8).

Table 1. Elements weight in AAN mix standard

Element/ compound	Conc. (mg/L)	Conc. (mg/L)	Dilution (x)	Final Conc. in 100 mL (mg/L)	Weight (µg) /100 µL	Note
As	10	-	-	-	1	ICP
Ca	1000	-	-	-	100	ICP
K	10	-	-	-	1	ICP
Mg	10	-	-	-	1	ICP
Na	10	-	-	-	1	ICP
Fe	100	-	-	-	10	ICP
Zn	100	-	-	-	10	ICP
Hg acetate	-	100	10	10	1	
NaCl	-	2000	10	200	20	Total Na= 21 µg
KCl	-	2000	10	200	20	Total K= 21 µg
$MgCl_3$	-	2000	10	200	20	Total Mg= 21 µg
$FeCl_3$	-	2000	5	400	40	Total Fe= 50 µg
$ZnCl_2$	-	2000	5	400	40	Total Zn= 50 µg

METHODS

Neutron Activation Analysis (NAA)

Materials needed were samples of rice flour and fish meal from APFAN, standard ICP mixed solutions from E. Merck, Standard Reference Material (SRM) NIST Rice Flour, SRM NIST Oyster Tissue, standard solution of Hg acetate 100 ppm, standard solutions: KCl, NaCl, $MgSO_4$ 7 H_2O, KCl and $ZnCl_2$ with concentration of 2000 ppm respectively and deionised water. Required equipments were: a set of spectrometer γ unit, analytical balance, 0.273 µL volume polyethylene vial, aluminum container, micro pipette, 100 mL measuring flasks and

Bandung Triga 2000 nuclear research reactor fascilities. Several steps start form washing vials up to quantitative analysis are as follows:

1) *Washing polyethylene vials*

   Polyethylene vials were soaked using 5N HNO_3 for 1 hour then rinsed using deionised water. The vial then checked using a neutral pH paper to examine the polyethylene vials were free from 5N HNO_3. Polyethylene vials were dried using infrared lights at 50 °C

2) *Preparation of multi-element standards*

   a. Into a 100 mL measuring flask added: standard solution of NaCl, KCl and $MgSO_4$ 7 H_2O as much as 10 mL respectively; standard solutions of $FeCl_3$ and $ZnCl_2$ 20 mL respectively, standard solution of Hg acetate as much as 10 mL. Deionised water was added up to volumetric mark then shake until mix standard solution is homogen.

   b. Mix standard solution in point a and a mix standard solution from ICP E. Merck were dispensed using 100 µL micro pipette into 100 polyethylene vials. The vials then dried using an infrared light at 50°C for 3x24 hours. The weight of each elements/100 µL presented in Table 1. The weight of multi element standard were in the range of elements contain in the sample.

3) *Sampel and SRM preparation*

   SRM is used to examine the validity of the method and treated as samples. In the poliethylene vial, SRM NIST Rice Flour, SRM NIST Oyster Tissue, rice flour and fish meal were weighed using an analytical balance of 50 mg in triplicate. For analysis of medium and long lived radioactive, samples and standards vial were covered by Al foil but not for the short lived radioactive nuclei.

4) *Short-lived ($t^{1/2} \leq$ 1 hour) irradiation*

   Standards and samples in polyethylene capsules were irradiated for 2 minutes in the pneumatic irradiation facility in Bandung Triga 2000 nuclear research reactor.

   After irradiation, samples and standards were measured using a γ spectrometer unit at a distance of 25 cm away from the High Purity Germanium (HPGe) detector for 200 seconds.

5) *Medium and long lived ($t^{1/2} \geq$ 1.5 days) irradiation*

   Samples and standards in aluminum capsules were irradiated on the reactor core facility at Bandung Triga 2000 nuclear research reactor for 3 days with a neutron flux of ± 3.6×10^{12} n/cm^2/second. Radioactive samples and standards were counted for 900 seconds for Na, K and As radionuclides with 3 days cooling time. The same samples and standards were continued counted for long lived radioactive nuclei (≥ 3 days) for 2000 seconds after 2 weeks cooling.

6) *NAA Quantitative Analysis*

   NAA quantitative analysis is a comparative method, it compares elements concentration in the sample to standards weight that have been known. The elements concentration in the sample is calculated using the formula:

$$C_s = \frac{W_{st}}{W_s} \times \frac{A_s}{A_{st}} \qquad (2)$$

   Where C_s=concentration of the element in the sample; W=weight of the sample and standard, A=activity of sample and standard. The activity for a particular radionuclide is calculated from this following equation:

$$A_t = A_0 \times (1 - e^{-\lambda t}) \qquad (3)$$

   Where A_t= activity in number of decay per unit time, A_0 = activity post irradiation, λ = decay constant and t = irradiation time.

Atomic Absorption Spectrophoto-metry (AAS)

A flame atomic absorption spectrometer technique (FAAS) SavantAA GBC with deuterium (D_2) background correction and flameless technique Graphite Furnace AAS (GFAAS) Agillent with Ziemen background correction were used as main equipments. Copper, calcium, cadmium, manganese, potasium, iron, lead and zinc hollow cathode lamps were used as light sources. Concentrations of Ca, Cu, Mg, K, Fe, Zn were determined by FAAS meanwhile Pb and Cd were measured by GFAAS. The instrumental parameters of AAS were listed in Table 2.

The GFAAS analyses were run in argon atmosphere as purging gas, in a pyrolitic graphite tubes. The sample volume injected to the furnace was 20 µL. Atomization program was obtained into 4 steps: drying, ashing, atomizing and cleaning. The concentration of the elements of both methods were obtained from a calibration plot. Steps in AAS method were:

1) *Washing apparatus laboratory*

   Laboratory glasswares was soaked overnight in 5 N HNO_3 solution. All of the glasswares then were washed with deionised water and dried. Deionised water was used throughout the experimental work.

2) *Sample digestion*

   Acid digestion is required for the metals determination by AAS. It was carried out according to a standard procedure using Milestone microwave digestion. Temperature and power digesting program was set at 160 °C with power 1000 Watt for 10 minutes. Sample digestion was performed in teflon vessels by following steps: about 1 gram of three replicates rice flour and fish meal were dissolved in 7.5 mL Merck nitric acid 65% suprapur and 2.5 mL deionised water. The digestates were evaporated till white fumes of nitric acid arose and sample volume were reduced up to 2–3 mL. The final volume was adjusted to 25 mL into a volumetric flask by adding deionised water. SRM NIST Rice Flour and Oyster Tissue and a series of blanks were prepared using the same digestion method.

Table 2. AAS instrumental parameter of Cu, K, Fe, Ca, Zn, Mg, Cu, Cd and Pb

Analyte ion	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Optimum working range of FAAS (mg/L)	Optimum working range of GF AAS (µg/L)
Cu	324.7	0.5	4.0	0.2–5	-
K	766.5	0.5	6.0	0.5–1.5	-
Fe	248.3	0.2	7.0	0.2–9	-
Ca	422.7	0.5	5.0	0.5-4	-
Zn	213.9	0.5	5.0	0.2–1.5	-
Mg	285.2	0.5	3.0	0.1–0.4	-
Cd	766.5	0.5	6.0	-	0.5–1.5
Pb	248.3	0.2	7.0	-	10-40

3) *Working standard solution*

FAAS working standard solution was made according to the optimum working range and elements contain in the sample by diluting standard stock solutions. Multi element working standard solution was used during the measurement. Standard stock of Cu, K, Mg, Fe and Zn except Ca were prepared to be a multi element working standard solution by diluting 10 times stock solutions of 1000.0 mg/L of these ions supplied by Merck in a 100 mL volumetric flask.

The concentrations 10 mg/mL of multi element working standard solution were made into 0.2; 0.4; 0.8; 1 and 1.5 mg/L by diluting 2; 4; 8; 10; 1 and 15 mL of this multi elements standard solution into a 100 mL volumetric flask then adjusted by adding 0.1N HNO_3 solution. Preparation of blank standard solution was using 0.1N HNO_3 solution. Single element working standar of Ca is prepared in the same way. The difference is, there was an addition of Sr 2000 mg/L as a releasing agent GFAAS working standard solution is made by means two concentrations 10 µg/L and 100 µg/L of cadmium and lead used as bulk concentrations to make working standard solution series. These working standard solution series were run under an auto mix program by Agillent. The total volume injected to the furnace was 20 µL equiped by an automation system. Table 3 below showed the automix program of Cd and Pb.

Table 3. The automix program of Cd and Pb

Rate based solutions	Conc. (µg/L)	Make up (µL)	Bulk std 10 µg/L (µL)
Cd			
Cal zero	0	20	0
Standard 1	0.5	19	1
Standard 2	1	18	2
Standard 3	1.5	17	3
Standard 4	2	16	4
Total volume 20 µL			
Pb			
Cal zero	0	20	0
Standard 1	10	18	2
Standard 2	20	16	4
Standard 3	30	14	6
Standard 4	40	12	8
Total volume 20 µL			

4) *AAS quantitative analysis*

The concentration (C) of each element, in mg/kg, was calculated as follow:

$$C = \frac{a \times V \times F}{m} \qquad (4)$$

Where C = concentration in the test portion sample (mg/kg), a = concentration (mg/L) in the element in the digest solution, V = volume (mL) of the test solution after being made up, F = dilution factor of the test solution, m = weight of the test portion (g).

Quality Control

Elements characterization using SRM is needed for data accuracy. In this activity, both methods using NIST SRM Rice Flour and Oyster Tissue. Examination of method validation was obtained by using two parameters those are accuracy and precision. Accuracy is expressed as percent recovery and calculated according to the equation as follow:

$$\%\text{Recovery} = \frac{\text{Concentration}_{\text{obs}}}{\text{Certificate Value}} \times 100\% \qquad (5)$$

Acceptance accuracy is shown in Table 4.

Table 4. Accuracy acceptance criteria

Concentration	Recovery (%)
100%	98-101
10%	95-102
1%	92-105
0,1%	90-108
0,01%	85-110
10 µg/g (10 ppm)	80-115
1 µg/g (1 ppm)	75-120
10 ng/g (10 ppb)	70-125

Precision parameter is stated as Horwitz precision (RSDr) from the equation below:

$$\mathrm{RSDr} = 2^{1-0.5\log C} \qquad (6)$$

where C is concentration fraction. For example: concentration fraction of ppm is 10^{-6}.

Precision acceptance is set by our laboratory as HorRat value as much as 0.3–1.3 as fully acceptable recommended range according to Association of Official Analytical Chemists (AOAC) (11). HorRat values is calculated below:

$$\mathrm{HorRat} = \frac{\%CV}{RSDr} \qquad (7)$$

Where % CV = % coefficient of variation.

RESULTS AND DISCUSSION

In this activity, verification as quality assurance for NAA and AAS were carried out by analysing elements in rice flour and oyster tissue from National Institut of Standards and Technology (NIST) presented in Table 5 and 6.

The accuracy parameter of the two methods from Table 5 and 6 were then compared with the acceptance criteria of accuracy in Table 4. Accuracy refers to how close a measurement is to the true value which is stated in percent recovery as a function of analyte concentration [11]. Based on Table 4, percent recovery of the two methods for Na, K, Ca, Mg, Fe, Cd, Hg and Pb in rice flour and oyster tissue in Table 5 and 6 were suitable with the percent recovery range values determined by AOAC.

HorRat values from Table 5 and 6 of the two methods were in the range 0.1 up to 1.3. It meant that precision of both method fullfilled the value as required by TAR laboratory. From Tables 5 and 6, concentration of all elements in SRM Rice Flour and Oyster Tissue gave a good agreement with the certificate values for both methods. These results showed that NAA and AAS are valid methods for Na, K, Ca, Mg, Fe, Cd, Hg and Pb in SRM rice flour and oyster tissue

Table 5. Verification of SRM rice flour dan Oyster Tissue using NAA

Parameter	Rice Flour				Oyster Tissue			
	Obs. mg/Kg	Cert. mg/Kg	%Rec.	HorRat	Obs. mg/Kg	Cert. mg/Kg	%Rec.	HorRat
Ca	124.9 ±10.9	118.4 ± 6	105	1.1	810 ±54	838 ± 20	97	1.1
Mg	565.2 ± 25.6	560 ± 20	101	0.7	1116 ± 80.6	1085 ± 23	103	1.3
K	1280 ± 50	1280 ± 8	100	0.7	6020 ± 275	6520 ± 9	92	1.1
Na	6202 ±325	6600 ± 8	94	1.2	3303 ± 160	3297 ± 5.3	100	1
As	0.32 ±0.03	0.29 ± 0.03	110	0.5	8.16 ±0.77	7.65 ± 0.65	107	0.8
Fe	7.53 ± 1.08	7.4 ± 0.9	100	1.2	208 ± 7.5	205.8 ± 6.8	101	1.2
Zn	18.73± 0.28	19.4 ± 0.5	100	0.1	1323 ± 4.6	1424 ± 46	93	0.7
Cu	-	2.35 ± 0.16	-	-	-	71.6 ± 1.6	89	1.2

Table 6. Verification of SRM rice flour dan Oyster Tissue using AAS

Parameter	Rice Flour				Oyster Tissue			
	Obs. mg/Kg	Cert. mg/Kg	%Rec	HorRat	Obs. mg/Kg	Cert . mg/Kg	%Rec	HorRat
Ca	119.4 ± 10.2	118.4 ± 3.1	101	1.1	838 ± 35	838 ± 20	100	0,6
Mg	488 ± 25	560 ± 20	88	0.8	1066 ± 44	1085 ± 23	98	0,7
K	1253 ± 37	1280 ± 8	98	1	6049 ± 245	6520 ± 90	93	1,1
Fe	6.8 ± 0.16	7.4 ± 0.9	91	0.2	193 ± 14.6	205 ± 6,8	94	1,0
Zn	19.4 ± 0.7	19.4 ± 0.5	100	0.4	1330 ± 59	1424 ± 46	93	1,0
Cu	2.11 ± 0.11	2.35 ± 0.16	90	0.4	63.90 ± 1.74	71,6 ± 1,6	89	0,3
Cd	0.025 ± 0.003	0.022 ± 0.002	112.4	0.4	2.35 ± 0. 13	2,48 ± 0,08	95	0,1
Pb		-			0.301 ± 0.038	0.308 ± 0.009	98	0.7

Tabel 7. Z-score interpretation

Z-score Value	Categories
≤ 2	Satisfactory
2 < x < 3	Questionable
≥ 3	Unsatisfactory

APFAN Proficiency Test 1 (APFAN PT 1) provides 2 commodities namely rice flour and fish meal. The parameters of both commodities were Na, K, Ca, Mg, Fe, Cd, Hg and Pb. The results of APFAN's elements characterization in rice flour and fish meal were divided into 3 categories of Z-scores, they were: satisfactory, questionable, and unsatisfactory results. These interpretation of Z-scores were presented on Table 7.

Elements of As, K, Ca, Mg, Na, Fe, Zn, Cd, Pb and Hg results in rice flour and fish meal using NAA and AAS were presented in Tables 8 and 9. NAA and AAS feature high accuracy and precision in the elemental characterization since the equipments and samples are adequately prepared. Both methods require several steps to present a valid testing report

Table 8. Rice flour metals analysis using NAA and AAS

Parameter	Conc. (mg/kg)		X_{pt}	Z-Score		Satisfactory Result		Questionable Result		Unsatisfactory Result	
	AAN	AAS		AAN	AAS	AAN	AAS	AAN	AAS	AAN	AAS
Na	37.9 ± 2.0	-	100.62 ± 2.74	-3,90	-	-	-	-	-	v	-
K	127 ± 17	123±11	99.9 ± 2.77	1,69	1,44	v	v	-	-	-	-
Ca	133±22.0	125±9.0	129.01 ± 3.32	0,20	-0,20	v	v	-	-	-	-
Mg	125±14.0	97.0±3.4	86.48 ± 2.34	2,88	0,79	-	v	v	-	-	-
Fe	-	13.7±4.6	10.65 ± 0.20	-	1,80	-	v	-	-	-	-
Cu	-	1.79± 0.13	1.580 ± 0.05	-	0.89	-	v	-	-	-	-
Zn	9.77±0.9	10.0±0.8	9.628 ± 0.20	0,12	0,32	v	v	-	-	-	-
As	0.169± 0.058	-	0.0088 ± 0.004	4,26	-	-	-	-	-	v	-
Cd	-	0.00690± 0.0018	0.006 ± 0.0003	-	0,90	-	v		-	-	-
Pb	-	0.115± 0.024		No statistic evaluation							
Hg	0.00379± 0.00088	-		No statistic evaluation							

Note: X_{pt}= assigned values of measurands for evaluation of testing parameters in rice flour

Table 9. Fish meal metals analysis using NAA and AAS

Parameter	Conc. (mg/kg)		$X_{pt\ (mg/kg)}$	Z-Score		Satisfactory Result		Questionable Result		Unsatisfactory Result	
	AAN	AAS		AAN	AAS	AAN	AAS	AAN	AAS	AAN	AAS
Na	6680± 30.0	-	7266 ± 410	-0.48	-	v	-	-	-	-	-
K	7340 ± 990	7470 ± 510	7245 ± 304	0.11	0.25	v	v	-	-	-	-
Ca	49100 ± 800	50600 ± 2600	59684 ± 2063	-1.81	-1.55	v	v	-	-	-	-
Mg	2780 ± 240	2980 ± 170	2601 ± 149	0.39	0.83	v	v	-	-	-	-
Fe	585 ± 78	637 ± 150	489.4 ± 22.2	1.19	1.84	v	v	-	-	-	-
Cu	-	5.27 ± 0.19	4.33 ± 0.2	-	1.58	-	v	-	-	-	-
Zn	109± 7.0	111 ± 4.0	92.20 ± 5.8	1.06	1.19	v	v	-	-	-	-
As	5.48 ± 1.24	-	5.055 ± 0.475	0.31	-	v		-	-	-	-
Cd	-	0.410 ± 0.104	0.208 ± 0.015	-	4.54	-	-	-	-	-	v
Pb	-	0.163 ± 0.037	0.743 ± 0.083	-	-2.21	-	-	-	v	-	-
Hg	0.0525±0.018	-	0.149 ± 0.011	-2.84	-	-	-	v	-	-	-

Note: X_{pt}=assigned values of measurands for evaluation of testing parameters in fish meal

These steps are preparation of equipments, samples and standards preparation, measurement, processing and data analysis. Contamination on the sample preparation stage must be avoided. It could avoid in several ways, firstly from washing equipments, the use of the reagents such as high purity nitric acid, deionised water and maintaining cleanliness laboratory facilities.

Washing is the first preparation stage that supports validity of the result. A 5N nitric acid solution is used in washing stage to dissolve the impurities attached to the container wall so it remains an acid-soluble ion. Deionised water with resistivity of 18.2 MΩ should be used in the analysis of trace elements. Neutron Activation Analysis is a very sensitive method therefore gloves must be used by the workers on sample preparation.

Another method, AAS, needs a homogenous sample solution to analyze elements in the sample. To avoid contamination and loss of volatile elements, samples were digested using wet digestion method in PTFE vessels with nitric acid 65% suprapur.

There are several nuclear analytical techniques. Two of them are NAA and X-Ray Fluorescence (XRF) which are National Nuclear Energy Agency (BATAN) main method in elements characterization. Figure 3 below presented methods characterization for severel elements Studied in this activity summarized from Suzy M. Juraja and Syukria Kurniawati (12, 13). Figure 3 showed that Cd prefers to neutron epythermal which is not Bandung Triga 2000 nuclear research reactor's neutron characteristic meanwhile Cu is characterized better using not only XRF but also AAS. SP Murarka et all studied that Pb more suitable analysed using Fast NAA (FNAA) which another type of NAA methods (14). These limitations caused Cu, Pb and Cd were obtained by AAS as a complimentary method.

Table 8 showed, NAA gave an unsatisfactory result for Na and As and questionable result for Mg. Fe was not reported for NAA because there was poor photopeak of ^{59}Fe in rice flour. A small amount concentration of Fe in rice flour caused decreased method sensitivy (1).

Figure 4 showed detection sensitivity for NAA. It could be seen that 0.53 µg Fe in about 0.05 g sample weight (Fe concentration in rice flour was 10,65±4.6 mg/kg according to APFAN's assigned value) caused concentration Fe in rice flour was in the instrument detection limit. Eventhough Fe concentration in rice flour is small but AAS gave better result than NAA because AAS sample weight much more than NAA. Based on the APFAN PT1 Report 2017, it was found only 42.5% of satisfactory results for the As element (15) were obtained from laboratories which implemented samples digestion preparation resulted in a homogenous sample solution using AAS, ICP-OES and ICP MS as method analysis.

From Table 9 fish meal metals analysis, the AAN method provides questionable results for Hg meanwhile AAS gave unsatisfactory and questionable result for elements Cd and Pb. Questionable results for Hg caused by a spectral interference from the 279.6 keV gamma ray of ^{76}Se which completely overlaps the 279.2 keV photopeak of ^{203}Hg (16). APFAN PT1 2017 reported that 50% of laboratories obtained satisfactory result for mercury were using Cold Vapor, ICP MS and Hg Analyzer (15).

To the questionable and un-satisfactory results, our laboratory applied a policy that for the two methods should be followed up for Na, As and Mg analysis in rice flour for AAN as well as Hg for AAN and Pb and Cd for AAS in fish meal. Method optimization such as flux neutron, sample weight, counting time and spectrum interference should be more paid attention for NAA in re-analysis not only for Na, Fe, As and Mg analysis in rice flour but also Hg in fish meal. For AAS, not only viscocity between samples and standards but also atomizing program optimization should be more paid attention in GFAAS for Pb and Cd in fish meal in re-analysis. Characterization of sodium, arsenic and mercury in rice flour and fish meal reported only from NAA because of its advantages compare to AAS not only in simple preparation but also they are have high probability with neutron thermal to have a nuclear reaction at Bandung Triga 2000 nuclear research reactor.

The results above showed that AAN presented good accuracy and precision of potassium, calcium and zinc in rice flour metals analysis meanwhile AAS gave satisfactory results for all elements reported in the same commodity. Fish meal metals analysis presented satisfactory results for sodium, potassium, calcium, magnesium, iron, zinc and arsenic for AAN. Satisfactory results for potassium, calcium, magnesium, iron, zinc and copper in the same commodity were obtained from AAS.

It could be stated that implementation of NAA and AAS on the rice flour and fish meal samples gave satisfied accuracy and precision results. Participation in APFAN PT 1 was intended to maintain our laboratory competency as a testing laboratory which has been accredited by Komite Akreditasi Nasional (KAN) since 2005

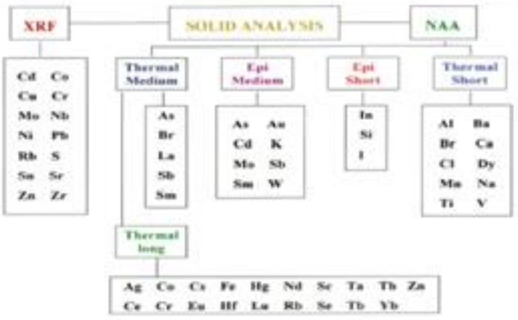


Figure 3. Summary elements characterization methods (12, 13)

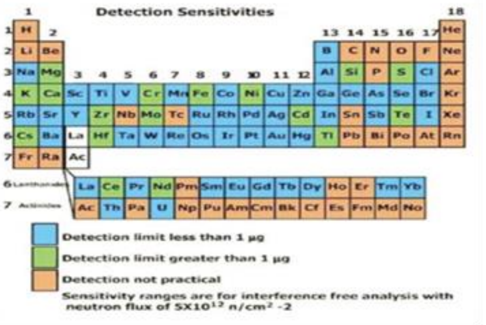


Figure 4. Detection sensitivities (1)

CONCLUSION

Base on APFAN's report, NAA and AAS had satisfactory result in rice flour where Z-score value of K, Ca, Zn < 2 meanwhile AAS gave Mg, Fe, Cu, Cd < 2 in the same sample. NAA gave the Z-score 2 < Mg < 3 in rice flour. Satisfied performance in fish meal gave Z-score values of K, Ca, Mg, Fe, Zn < 2 for both of them. Values of Na < 2 and 2 < Hg < 3 obtained from NAA in fish meal and Z-score of As was < 2 with NAA. Moreover, 2 < Pb < 3 obtained from AAS in fish meal sample. These results showed that NAA and AAS are accurate and precise methods on food analysis in rice flour and fish meal from APFAN to maintain laboratory competency.

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