Iodine analysis of foodstuffs samples using epithermal instrumental neutron activation analysis

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Abstract. Iodine is an essential element that has an important role in the proper growth and thyroid hormone functioning of humans. Iodine deficiency was correlated with the health status of human-caused by malnutrition. The analytical method to analyze the Iodine content on foodstuffs is limited because Iodine concentration exists in a level of a trace. $^{127}$I has a ratio of I to $\alpha$ relatively high, and it is possible to obtain $^{128}$I ($t_1/2 = 24.5$ minutes) using nuclear reaction with an epithermal neutron. Samples were collected at Magelang region, and it consists of foodstuffs that consumed by the citizen. All sample has been dried using Freeze dryer at $-90^\circ$ C and 0.03 bar for 24-48 hours. After drying, the sample then pounded to get the form of granules smooth, about 100-150 mesh. About 40 to 130 mg of sample was weighed accurately on a clean micro vial of Polyethylene. Irradiation has been carried out at 15 MW reactor power using neutron epithermal for 45 seconds at the rabbit facility of GA. Siwabessy reactor. After cooling 5 to 10 minutes, the irradiated sample then counted for 300 seconds, and the gamma-ray spectra obtained emitted have been analyzed by Hyperlab software. Several standard reference materials of NIST have been used as analytical quality control. The experimental result shows that the Iodine has the Boron ratio, R$_B$, and the Advantage factor, F$_adv$, equal to 2.4 and 21, respectively. Trace element of Iodine has been determined quantitatively on nine spices, seven types of meat, and 32 vegetables. The Iodine concentration on spices have average $1.57 \pm 0.23$ mg/kg with range value 0.38 mg/kg to 3.4 mg/kg. Iodine on vegetable have average of $2.00 \pm 0.43$ mg/kg with range value of 0.38 mg/kg to 7.30 mg/kg. Meanwhile, its concentration on meat has range 0.71 mg/kg to 2.16 mg/kg, with an average of $1.44 \pm 0.28$ mg/kg, lower than that on vegetables. Epithermal INAA is a reliable analytical technique for Iodine determination quantitatively.

1. Introduction
Iodine is an essential element that has a vital role in the proper growth and thyroid hormone functioning of the human body [1][2][3]. Iodine deficiency was correlated with the health status of human-caused by malnutrition [1]. The Iodine deficiency disorder (IDD) will cause autism, the goiter, late development of intelligence in the brain and mental baby, decreasing one's IQ level, decrease the body's fertility level, an occurrence of hypothyroidism and the risk of a miscarriage of the womb [1]. The daily dietary intake of iodine, as recommended by WHO is 50-200 $\mu$g for infants to adults [4].

In Indonesia nowadays, the primary source of iodine intake comes from the consumption of sea fish and salt consumed with iodine. Data on the proportion of Indonesians who consume marine fish is 42.6%, with an average consumption of marine fish per person per day of 25.5 gr. Iodine's nutritional
needs can be met by varying the types of food consumed. It is necessary to diversify consumption patterns not only for fish but also for various plants containing Iodine.

Iodine concentrations in consumption food, both marine and food products, are deficient in the μg order (typically < 1 μg/g). It is one of the difficulties for the identification and quantification of these elements and therefore requires specific, accurate, and sensitive analytical methods. Chemical methods in the determination of Iodine have been published include ICP-MS[5][6][7][8] and ion chromatography[9][10]. The determination of Iodine by chemical method involves the stage of destruction and dissolution [11]. This stage is a very crucial stage for the analysis of trace elements because of the potential for cross-contamination or disappearance during considerable process. For trace elemental analysis, such chemical processes potentially will reduce the accuracy of the measurement results. This can be caused by the loss of iodine during the chemical treatment process, such as dissolution, and the occurrence of cross contamination from solvents. Chemical methods are recognized to have an advantage in fast analysis time and are relatively independent of others. From that place, the development of an analytical method with high sensitive and non-destructive is required.

One alternative to the determination of iodine trace elements is to use nuclear techniques[2][12][13][11]. This technique is developed by countries that have nuclear reactors as providers of neutron sources. Thermal neutrons have been widely used to determine trace elements in different types of samples, via the Instrumental Neutron Activation Analysis (INAA) method. Unfortunately, the use of thermal neutrons for Iodine analysis in samples containing high Na, Cl, Br, Mg, and Mn elements is difficult because of the high Compton background generated by the thermal neutron interaction with these elements. The use of epithermal neutrons for Iodine determination is very advantageous based on the nuclear properties of Iodine and can also suppress the formation of Compton background[14]. The 127I has a ratio I, to σ relatively high, and it is possible to activate with the epithermal neutron. Utilization of epithermal neutron will reduce significantly a Compton background cause by 23Na(n,γ)Na, 35Cl(n,γ)Cl, 24Mg(n,γ)Mg and 82Br(n,γ)Br which produced by thermal neutron reaction. In this research, Flexi-boron is used to absorb the thermal neutron, so that interacting with the target nucleus is an epithermal neutron. The goal of this work is to obtain the nuclear analytical method for trace Iodine analysis on the biological sample. The scope of this work is the determination of ratio boron, R, and Advanced Factor, F₂, for Iodine, determine the best condition for trace Iodine element, validation and quantitative determination of Iodine on some biological samples.

2. Methodology

The detail method of the utilization Cd and Boron filter at lower power have been reported. The foodstuff samples have been collected from the Magelang area using the market-based method. It consists of six types of meat samples, 35 samples of vegetables and seven types of spices. While for R, and F₂ determination, the Standard reference materials of NIST 1548a Typical Diet have been used.

About 50 mg of dry sample was weighted on cleaned 0.7 mL micro Vial (Cole Parmer, Polyethylene, 983 mg/L) and was sealed using a hot glass rod. Than target placed inside Flexi-Boron (Shieldwerx USA, 25.3% Boron isotope) filter [6]. We used 3.4 mm thick formed a cylindrical shape with bottom and top discs to completely enclose the target inside the Polyethylene capsule, Figure 1. Irradiations have been carried out at the irradiation channel of the rabbit system for 60 seconds at a reactor power of 15 MW.

The result of induced nuclear reaction was measured using a high-resolution HPGe detector (Canberra, Coaxial type, Resolution of 1.99 keV at 1332.4 keV of 57Co, P/C=40) after 10 minutes cooling time for 300 seconds counting time. The gamma-ray spectrum obtained was analyzed using Hyperlab software. Table 1 show some nuclear data of selected element used on this work.

R, of isotope for specific channel irradiation was calculated using the following equation, where A and A, are activity obtained with and without Boron filter respectively, σ is thermal cross-section, φ, and φ₂ are thermal and epithermal neutron flux respectively, I is resonance integral. The advantage
factor, $F_{Na}$, was calculated using equation (2). This factor has been calculated based on Na contaminant as a major element interferes with Compton background.

$$R_B = \frac{A}{A_B} = \frac{\sigma_{th} \cdot \phi_{th} + I_0 \cdot \phi_{epi}}{I_0 \cdot \phi_{epi}} = \sigma_{th} \cdot \phi_{th} + 1$$

(1)

$$F_{avg} = \frac{(R_B)_{Na}}{(R_B)_{Elements}}$$

(2)

Iodine concentration was determined using a comparative method based on standard reference material. This concentration was calculated using equation,

$$[I]_{Sample} = m_{std} \cdot \frac{cp_{Sample}}{cp_{Standard}} \cdot \frac{D_{Standard}}{D_{Sample}} \cdot \frac{1}{w_{Sample}}$$

(3)

Where $[I]_{Sample}$ is Iodine concentration in the sample, $m_{std}$ is mass of Iodine in the standard used, $cp_{Sample}$ and $cp_{Standard}$ were count rate for the sample and standard respectively, $D_{Standard}$ and $D_{Sample}$ were Decay factor for standard and sample respectively, and $w_{Sample}$ is the weight of the sample.

Figure 1. Flexi-boron neutron thermal filter used (left) and target configuration on polyethylene capsule (right).

Table 1. Some nuclear properties for selected elements of Br, Cl, I and Na [15].

| Target isotope | Activation product | Isotope abundance, % | Half-life* | $\sigma$ [barns] | $I_0$ [barns] | $E_f$ keV(%) |
|----------------|-------------------|----------------------|------------|-----------------|--------------|--------------|
| $^{127}$I      | $^{125}$I         | 1.000                | 24.9m      | 4.04            | 100          | 442.9 (16.90) |
| $^{23}$Na      | $^{24}$Na         | 1.000                | 14.96h     | 0.513           | 0.303        | 1368.60 (100) |
| $^{81}$Br      | $^{80}$Br         | 0.493                | 17.68m     | 2.58            | 49.8         | 616.30 (6.70) |
| $^{37}$Cl      | $^{35}$Cl         | 0.242                | 37.24m     | 0.423           | 0.29         | 1642.69 (31.00) |
3. Result and discussion

The effect of heat and gamma radiation exposure due to the use of Cd for Epithermal INAA on the rabbit system is one of the difficulties in the development of INAA Epithermal in the GA Siwabessy rabbit reactor system. Boron material, as Flexi-boron, is one of the substitutes for Cd that can be used for INAA Epithermal on the rabbit system. The boron will produce less heat than Cd, making it easier to handle. The boron also has wider Cut-off energy compared to Cd. The use of Boron filters for short irradiation in the hydraulic rabbit system of RSG Siwabessy reactor is very beneficial because the heat generated can still be anticipated by the cooling water system. Thereby the possibility of melting on target can be avoided. Cut-off energy for B (~10 eV for ~3.4 mm thickness) is higher compared to Cut-off energy for Cd (0.5 eV) that mean more element will be evaluated. Figure 2 below shows the comparison of two gamma rays of Iodine spectra obtained without Flexi-Boron filter (above spectra) and with 3.4 mm thickness of Flexi-Boron cover (below spectra) as previously published. The utilization of Flexi-boron will reduce significantly the Compton background more than ten times lower. In spectra A, we are difficult to locate a gamma peak of 443.9 keV for $^{128}$I, but in spectra B, the $^{128}$I could be identified. High Compton background produced by $^{23}$Na($n$,γ)$^{24}$Na nuclear reaction can be reduced significantly.

![Gamma spectra](image)

Figure 2. Gamma-spectra of Iodine at Typical Diet sample using thermal neutron without filter (top) and using a filter of Flexi-boron (below). Target was irradiated on PE capsule at reactor power of 15 MW for a 2-minute irradiation and cooling time of 5 minutes.

The advantage factor, $F_{Adv}$, represents the degree to which the particular interference will be reduced by using the shield since Na is the primary source of Compton background beside Cl, Br, and Mn. The Na element was used as a reference source of interference in $F_{Adv}$ calculation. Table 2 shows the results of the determination of $R$, and $F_{Adv}$ for Cl, I, Na and Br, compared with the data in the publication. The experimental result shows that the Iodine has ratio Boron, $R_B$, and Advantage factor, $F_{Adv}$ equal to 2.4 and 21, respectively. This result obtained was a relatively good agreement with the value given by Stuart and Bhagat.

| Target isotope | Activation product | $R_B$ | $F_{Adv}$ |
|---------------|-------------------|-------|----------|
| $^{127}$I     | $^{128}$I         | 2.1   | 2.7      |
| $^{23}$Na     | $^{24}$Na         | 40.8  | 69.9     |

Table 2. Boron ratio, $R_B$, and advantage factor, $F_{Adv}$ using boron filter at the rabbit system of GA. Siwabessy reactor.

*Note : m=minutes, h=hours

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Validation of Iodine analysis using Epithermal INAA has been done using several standard reference materials, and it has been published earlier [17]. The analytical result shows the result obtained was close to the certified value and close to some published data. In this work, Iodine concentration has been determined at 48 samples collected from Magelang area. The food samples have been divided into three groups; they were 32 vegetables, nine spices, and seven types of meat groups. Figure 3 below shows the Box-Whisker graph to compare the Iodine distributor at vegetables, meat, and spices. The average Iodine concentration in vegetables is relatively higher compared to the content of Iodine in meat and Spices, which is around two mg/kg, but with a relatively wide range of variants. The average concentration of Iodine in spices and meat is relatively the same, about 1.8 mg/kg.

![Box-Whisker graph showing Iodine distribution in vegetables, meat, and spices.](image)

**Figure 3.** Iodine distribution spices, vegetables and meat samples were taken from the Magelang sampling site.

The distribution of Iodine in spices shown in Figure 4 ranged from 0.38 mg/kg in Red onion (*Allium cepa L*) (to 3.40 mg/kg in Turmeric (*Curcuma longa*). The average of Iodine concentration was $1.57 \pm 0.23$ mg/kg.

![Iodine concentration in spices.](image)

**Figure 4.** Iodine distribution in spices sample taken from the Magelang sampling site.
The Iodine content on vegetables varied from 0.68 ± 0.14 mg/kg in Eggplant (*Solanum melongena*) to 7.30 ± 1.47 mg/kg in Pea (*Pisum sativum*) with an average value of 2.00 ± 0.43 mg/kg. The Iodine obtained in Pea and Tomato (*Solanum Lycopersicum*) samples relatively higher among vegetable samples. Data Iodine in Tomato, Lettuce (*Lactuca sativa*), and Cabbage (*Brassica oleracea*) have found 0.60 mg/kg and 1.1 mg/kg and 0.9 mg/kg respectively. Iodine concentration in all types of rice (*Oryza sativa*) was about 1 mg/kg. This value is slightly higher than that has been published. The Iodine contains on rice was in the range of 0.11 mg/kg to 0.99 mg/kg[5][18]. Figure 5 shows the distribution of Iodine in selected vegetables.

![Iodine distribution in vegetables](image)

**Figure 5.** Iodine distribution in the vegetable sample taken from the Magelang sampling site.

Meanwhile, Iodine content in meat has a range of 0.9 mg/kg – 1.6 mg/kg, and in fish marine has a range of 2.1 mg/kg to 2.2 mg/kg, lower than that on vegetables (Figure 6). Data publication shows that the range concentration of Iodine in meat was 0.002 mg/kg to 0.155 mg/kg, and in fish marine was 0.08 mg/kg to 1.60 mg/kg[5]. The Iodine concentration obtained on both meat and fish marine was slightly higher than the published value.

![Iodine distribution in meat](image)

**Figure 6.** Profile distribution of iodine in meat.
The use of Flexy-boron is quite effective and efficient for the determination of trace elements of iodine in food, compared with conventional chemical methods that require chemical treatment first. This neutron filter can suppress the background of Compton. Determination of Iodine in a food sample, through $^{128}$I which has a half-life of 24.99 minutes, was done through short irradiation with 10-15 minutes of cooling time, allowing the analysis to be carried out quickly. The use of a low sample number, around 50 mg, indicates this method is quite sensitive, accurate and competitive to the chemical method.

4. Conclusion
Epithermal INAA using Flexi-Boron as a thermal neutron filer has been used and optimized at the rabbit facility of the GA Siwabessy reactor. The Boron ratio, $R_B$ and Advantage Factor to Boron, $F_{adv}$, for the selected element of Iodine and Sodium have been determined and used to determine Iodine on foodstuffs. The $R_B$ of Iodine was lower than $R_B$ of Na and $R_B$ of Cl; meanwhile, the $F_{adv}$ of Iodine was high enough than the other. In general Iodine can be quantified using Epithermal INAA using Boron-filter. Iodine concentration in foodstuffs consists of vegetables, spices and meat, which have been analyzed. The Epithermal INAA is a reliable technique for trace Iodine analysis in foodstuffs.

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References
[1] Mahdiya Izati I and Mahmudiono T 2017 Iodine and Goitrogenic Intake among School Children in Ponorogo *Amerta Nutr.* 1 88–97
[2] Acharya R, Reddy a V R, Division R, Bhagat P R, Rajurkar N S and Sarathi D P Food Products By Epithermal Neutron 201–4
[3] Aryastami N K, Susilowati D and Usman Y 2011 Iodine salt consumption in Indonesian households : Baseline Health Survey 2007 *Bull. Penelit. Sist. Kesehat.* 14 160–6
[4] Kartono D, Hardinsyah, Jahari A, Sulaeman A, Astuti M, Soekatiri M and Riyadi H 2012 Ringkasan - Angka Kecukupan Gizi ( AKG ) yang dianjurkan bagi Orang Indonesia 2012 *Res. Gate* 1–18
[5] Haldimann M, Alt A, Blanc A and Blondeau K 2005 Iodine content of food groups *J. Food Comp. Anal.* 18 461–71
[6] Leufroy A, Noël L, Bouisset P, Maillard S, Bernagout S, Xhaard C, Vatheire F De and Guérin T 2015 Determination of total iodine in French Polynesian foods : Method validation and occurrence data *FOOD Chem.* 169 134–40
[7] Jer A, Ja R, Kacjan N, Germ M, Helena Š and Stibilj V 2018 Determination of iodine in plants by ICP-MS after alkaline microwave extraction 137 355–62
[8] Judprasong K, Jongjaiithet N and Chavasit V 2016 Comparison of methods for iodine analysis in foods *Food Chem.* 193 12–7
[9] Bla A, Makarewicz A, Korona-glowiak I and Dolliver W 2016 Journal of Trace Elements in Medicine and Biology 34 32–7
[10] Peng B, Wu D, Lai J, Xiao H and Li P 2012 Simultaneous determination of halogens ( F, Cl, Br, and I ) in coal using pyrohydrolysis combined with ion chromatography *Fuel* 94 629–31
[11] Bhagat P R, Pandey A K, Acharya R, Nair A G C, Rajurkar N S and Reddy A V R 2007 Selective preconcentration and determination of iodine species in milk samples using polymer inclusion sorbent *Talanta* 71 1226–32
[12] Andráši E, Kučera J, Bélavári C and Mizera J 2007 Determination of iodine in human brain by
epithermal and radiochemical neutron activation analysis. *Microchem. J.* **85** 157–63

[13] Sheyin F T, Oladipo M O A, Jonah S A and Sadiq U 2015 Elemental Analysis of Some Nigerian Food Legumes by k o-ENAA and INAA 241–51

[14] Zhang W, Bureau R P and Chatt A 2013 Epithermal instrumental neutron activation analysis in conjunction with anti-coincidence gamma-ray spectrometry for investigating iodine levels in Canadian foods Epithermal instrumental neutron activation analysis in conjunction with anti-coincidence gam *J. Radioanal. Nucl. Chem.* 495–501

[15] De Corte F 1987 The k0-standardization method: a move to the optimization of neutron activation analysis, Habilitation Thesis, University of Gent, Belgium

[16] STUART D C and RYAN D G 1981 Epithermal neutron activation analysis with a SLOWPOKE nuclear reactor *Can. J. Chem.* **59** 1470–5

[17] SUTISNA S, ALFIAN A, SUPRAPTI S and MUSTOFA K 2013 Quantitative Determination of I, Cl and Br on Biological Standard Reference Material using Epithermal Instrumental Neutron Activation Analysis Prosiding Seminar Nasional TAN 2013 pp 23–9

[18] Parengam M, Judprasong K, Srianujata S and Jittinandana S 2010 Journal of Food Composition and Analysis Study of nutrients and toxic minerals in rice and legumes by instrumental neutron activation analysis and graphite furnace atomic absorption spectrophotometry *J. Food Compos. Anal.* **23** 340–5