QUANTITATIVE DETERMINATION OF I, Cl AND Br ON BIOLOGICAL STANDARD REFERENCEMATERIAL USING EPITHERMAL INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

Concentration of Iodine (I), Chlorine (Cl) and Bromine (Br) at biological standard reference materials (SRM) have been determined using epithermal instrumental neutron activation analysis (EINAA).A number of 50-75 mg of SRM NIT 1548a Typical Diet, NIST SRM 1515 Apple Leave, BCR 063r Skim Milk Powder and SRM NIST 1573a Tomato Leaves were weighed at cleaned microvial. Cd-foil of 0.7 mmthick have been used to cover the sample and to absorb a thermal neutron. Irradiation has been carried out at RS03 rabbit position of GA. Siwabessy reactor for 30-40 second at 5MW power reactor. I, Cl and Br have been analyzed quantitatively using a comparator method through $^{127}I\ (n,\gamma)\ ^{128}I$,$^{37}Cl\ (n,\ \gamma)^{38}Cl$ and$^{79}Br\ (n,\gamma)\ ^{80}Br$ nuclear reactions. Those elements have been evaluated throughthe gamma peak of 443.9 keV, 1642.2 keV and 616.8 keV respectively. The result showed that Cd foil could reduce significantly a Compton background, up to 10 time lower compare to without used Cd filter. The analytical results of I and Cl are close to the certificate value with ratio of experimental result to certificate value is 0.91 – 1.06 while for Br 0.85-0.90.Iodine, Chlorine and Bromine at biological sample could be determine quantitatively using Epithermal INAA.

Keyword: Epithermal NAA, SRM, nuclear reaction.

ABSTRAK

Konsentrasi unsur-unsur Iodium (I), Khlor (Cl) dan Brom (Br) dalam bahan acuan standar biologi telah ditentukan menggunakan analisis aktivasi neutron epithermal Instrumental (AANEI). Sejumlah 50 – 70 mg bahan acuan standar SRM NIST Typical Diet, SRM NIST Apple Leaves, SRM NIST Tomato Leaves dan IRMM BCR 063a Skim Milk Powder ditimbang dalam vial mikro yang telah dibersihkan. Keping Cd setebal 0,7 mm digunakan untuk menutupi cuplikan danuntuk menyerap neutron termal. Iradiasi dilakukan di RS03 fasilitas rabbitRS03 reaktor GA. Siwabessy selama 30-40 detik pada daya reaktor 5 MW. I, Cl dan Br telah dianalisis secara kuantitatif menggunakan metode komparator terhadap bahan acuan lain yang mempunyai matrik dan komposisi relatif sama, melalui reaksi nuklir$^{127}I(n,\gamma)^{128}I$,$^{37}Cl(n,\ \gamma)^{38}Cl$ and $^{79}Br(n,\gamma)^{80}Br$. Unsur-unsur tersebut diidentifikasi masing-masing melalui energy 442,9 keV, 1542,2 keV dan 616,6 keV. Hasil menunjukkan bahwa penggunaan keping Cd dapat mereduksi latar belakang Compton secara signifikan, sekitar 10 kali lebih rendah relative dibandingkan dengan kondisi tidak menggunakan penutup keping Cd. Hasil analisis I dan Cl sesuai dengan nilai sertifikat dengan ratio 0.91 – 1.06, sementara untuk Br mempunyai kisaran 0.85-0.90. Dapat disimpulkan bahwa I, Cl dan Br dapat dikuantifikasi dengan baik menggunakan AANIE.

Kata kunci : Epitermal NAA, SRM, reaksi nuklir.

INTRODUCTION

Iodine is an essential trace elements needed by human body. Iodine deficiency is a major problem for the most of the population of Indonesia [1]. Iodine is required by the body in the formation of thyroxine hormone to regulate growth and development from fetal to adult [2-4]. The imbalance in the consumption of iodine have potentially leading to a variety of disorders, including cancer and abnormal growth and development of infants [1-4].

Determination of Iodine is conventionally performed by titration or colorimetric method involving destruction stages to convert into a liquid form [5]. This stage proved to be a very critical stage due to the possibility of cross-contamination, both of the reactants and of the environment, is quite height. Loosing during destruction stage also should beconsidered carefully because some iodine organic compounds is volatile [4]. This is very important to consider because a halogen compound exist at nature is very small, at level of sub-ppm (μg/kg).

The use of neutron activation analysis technique in the quantification of iodine, and others halogen elements, in various biological samples witha thermal neutrons havealso a variety of obstacles. High content of Sodium (Na), Manganese (Mn) and Chlorine (Cl) is the main contribution to the background count of Compton, and this could not be resolved by considering the decay time. Half-life of Iodine (^{128}I, $t_{1/2}$ = 24.99 min) is much lower than that of Na (^{24}Na , $t_{1/2}$ = 14.96 hours).Landsberger [6] and Canions [7] have used the Compton Suppression counting system or combination The Compton Suppression and Epithermal Neutron Activation Analysis.

El-Ghawi [2],Tobier L [8], E Andrasi [7] and Chien [10]have used epithermal neutrons to determine iodine in biological sample, while utilization of radiochemical neutron activation analysis have been publicated also [3,4]. The use of epithermal neutrons for the analysis of various elements, have been also reported by Stuart [11] and Seydou [12]. They showed that the use of epithermal neutron can reduced the Compton effects caused by ^{24}Na produced from ^{23}Na(n,γ)^{24}Na nuclear reaction.

The use of irradiation channels that equipped with a neutron absorber Cd layer have already widely used, especially for the reactor types of Triga Mark [4, 9] or Slowpoke [2, 12]. However, it is a few publications of the use of filters on the thermal neutron irradiation capsule for high flux reactor types. We have already modified the rabbit system using Cd filter to absorb the thermal neutron and used it for Epithermal INAA.

The aim of this research is to determine I, Cl and Br concentration containedon a number of biological standard references materials to validate the EINAA method at GA. Siwabessy multipurpose reactor.

METHOD

A number of 50-70 mg of biological standard reference materials on Table 2 was weighed on cleaned 1.7 mL micro Vial (Cole Parmer, Polyethylene, density of 983 mg/L) and was sealed using hot glass rod. As a standard comparator, it has been used other standard reference materials which have a matrix and similar composition [9]. All standards and samples were placed together inside Cd capsule, which have a thickness of 0.7 mm (Figure 1).

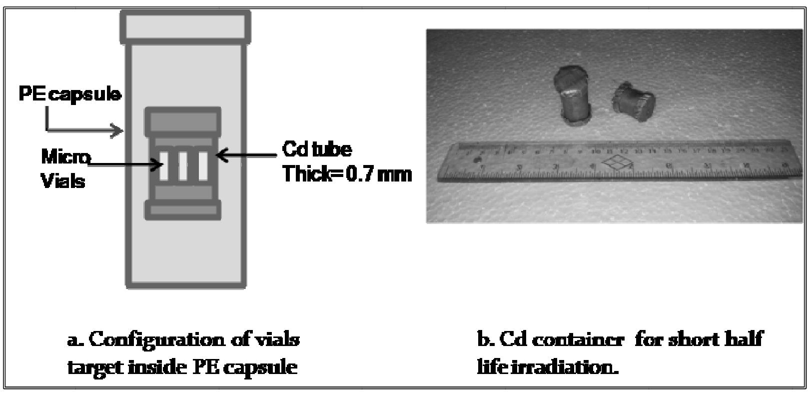

Figure 1. Cd irradiation container to determine a short half-life nuclides using EINAA at 5 MW reactor power.

Short irradiations have been carried out at RS03 of rabbit system for 300 second at areactor power of 5 MW. The results of epithermal induced nuclear reaction were counted using a high-resolution HPGe detector (Canberra, Coaxial type, Resolution of 2.0 keV at 1332.50 keV of ^{60}Co, P/C=40) coupled to the multichannel analyser (MCA) of Multiport II from Canberra. Counting time was 300-600 secondsafter 5 minutesdecay time to let ^{23}Ne at 439.9 keV decay ($t_{1/2}$ is 37.24s) [2]. The obtained gamma spectrawere analysed using PC-Hypermet from Institute of Isotopes, Kfki Atomic Energy Research Institute, Hungary [11].

Elemental quantification of I, Br and Cl have been done using a comparative method of Epithermal Neutron Activation Analysis (ENAA) as proposed by Liponen [9] and El-Ghawi [6]. Gamma energy peaks of 442.9 keV, 616.2 keV and 1642.4 keV has been selected to quantify of I, Br and Cl elements respectively. Table 1 show the used nuclear parameter in this work. While Table2 show the biological standard materialshave been used as quality control of analytical result.

Table 1. Nuclear Parameter of^{128}I, ^{38}Cl,^{80}Br,^{23}Naand ^{56}Mn used on the analysis by using epithermal neutron [14]

Radionuclides	Nuclear reaction	I_o/σ_o	Half-life (minutes)	$E\gamma$ (I_γ), keV
^{128}I	^{127}I(n,γ)^{128}I	24.8	25.0	442.9(16.9)
^{38}Cl	^{37}Cl(n,γ)^{38}Cl	0.69	37.3	1642.4(31.0),2167.5(42.0)
^{80}Br	^{79}Br(n,γ)^{80}Br	11.0	17.7	616.2(6.7)
^{24}Na	^{23}Na(n,γ)^{24}Na	0.59	897.5	1368.6(99.99), 2754.0 (99.88)
^{56}Mn	^{55}Mn(n,γ)^{56}Mn	1.05	154.7	846.8(98.8), 1810.7(27.2), 2113.1(14.3)

Table 2. Matricesof biological standard references materials (SRM) used from NIST and IRMM.

Standard Reference Materials	Matrices
SRM NIST 1548a Typical Diet	Foodstups
SRM NIST 1515 Apple Leaves	Biological material
CRM IRMM BCR 063a Skim Milk Powder	Food
SRM NIST 1573a Tomato Leaves	Biological material

RESULT AND DISCUSSION

Epithermal INAA (EINAA) have been developed at rabbit system of GA. Siwabessy reactor to be used on the quantitative analyse a short half-life radionuclides, especially for Iodine determination on biological sample. Table 3 show the performance and experimental condition of EINAA at a rabbit facility. The exposure radiation on surface of irradiated capsule reached of about 400 mRem. After cooling time of about 5 minute, the radiation expose will decrease to 200-300 mRem where we can open the capsule and safe in 1 minute. After encapsulated, the irradiated sample than counted at a level one of detector (42 mm distance) and the dead time obtained was about 1%. This mean that induced reaction of thermal neutron and the Cd foil will produced a high activity.

Gamma heating and high activity caused by irradiated Cd foil should be considered carefully because the experiment carried out at high flux reactor. The gamma heating will influence the physical properties of vial container, while the high activity on the surface will affect the handling of irradiated target.

Utilization of 0.7 mm thick Cd foil will filtered all neutron energy below energy cut-of Cd (~0.55 keV), and only neutron with energy greater than 0.55 eV will interact with atoms inside the capsule. Regarding to the Table 1, the epithermal neutron cross-section (equal to I_o/σ_o) of ^{127}I is greater than that for ^{23}Na, more than 40 times, and for ^{55}Mn not less than 25 times. This means, the induced nuclear reaction of epithermal neutron with ^{127}I nucleus theoretically will be greater chances compared to ^{23}Na nucleus, as well as ^{55}Mn nucleus.

Figure 2 show the comparison of two gamma ray spectras of SRM NIST 1548a Typical Diet obtained without Cd cover (spectra A) and other with 0.7 mm thick Cd-cover (spectra B). The irradiation have been carried out at 5 MW for 40 seconds. Compton high background in the spectrum of A, due to the macro elements Na, Cl and Mn in Typical Diet.NIST SRM 1548a Typical Diet contain major elements of 0.8% Na, 1.2% of Cl, 0.7% of K will produce the Compton background from ^{23}Na(n,γ)^{24}Na, ^{37}Cl(n,γ)^{38}Cl and ^{41}K(n,γ)^{42}K nuclear reaction respectivelly. In this condition, it was not possible to determine a trace element of Iodine through ^{128}I with a thermal neutron.

Table 3. Performance of Cd-foil as a thermal neutron filter for Epithermal Instrumental NAA at GA. Siwabessy reactor.

Power	Filter	T_i	T_d	T_c	Note
15 MW	Cd-foil, 0.7 mm thick	20 s	5 m	120 s	High activity 800 mRem on surface, Overheating, vial melt observed, Cd-foil broken.
5 MW	Cd-foil, 0.7 mm thick	120 s	5 m	120 s	600 mRem, Overheating, some vial melt.
		30-40 s	5 – 10 m	300 s	200-300 mRem, no vial melt observed

Note : s = second; m=minutes; T_i=irradiation time, T_d=decay time; T_c=counting time

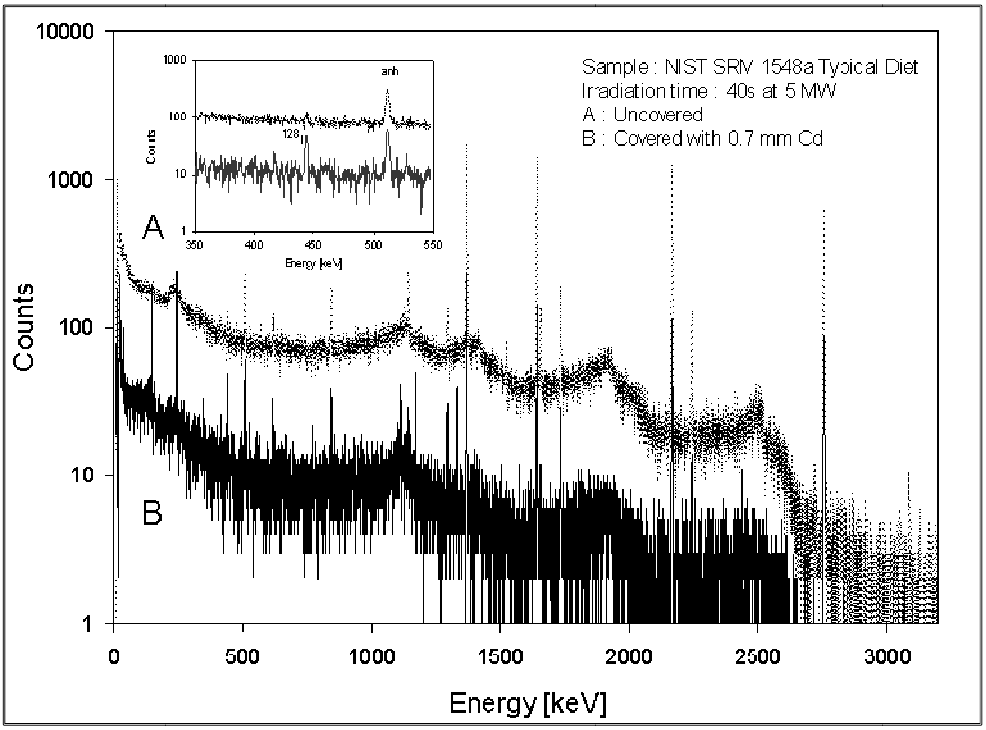

Figure 2. Comparison of epithermal to thermal neutron on activation analysis for ^{128}I quantification

Utilization of Cd foil could reduce the Compton background by ten times. In normal condition it is impossible to determine Iodine through ^{128}I (Eγ = 442.9 keV), but using Cd covered, the Iodine could determine quantitatively. The Cd foil will reduce significantly the Compton background more than 10 time lower. In spectra A we cannot identified gamma peak of 443.9 keV of ^{128}I, but in the spectra B, the ^{128}I could be identified quantitavelly.

Determination of short half-lived isotopes with ENAA using Cd filter on the power of 5 MW is still not a good idea. Heat and high radiation exposure are an obstacle in the irradiated sample handling. However, for the initial phase, we tried to calculate Br, Cl concentration and Iconcentration contain on biological reference material as show on the Table 2, and the results were compared to the certificate value to determine the feasibility of the analysis. Irradiation for 40 seconds is enough to identify Iodine, but not enough to determine the statistical uncertainty.

Table 4. Iodine content of Biological Reference Material determined using ENAA at 5 MW with Cd foil as filter

SRM/CRM	N	Concentration in mg/kg			
		This work	Certificate	Ratio**	Literature
NIST SRM 1548a Typical Diet	7	0.791 ± 0.120	0.759 ± 0.103	1.04	0.641 ± 0.044[7] 0.718 ± 0.027[9] 0.768 ± 0.200[13]
NIST SRM 1515 Apple Leaves	7	0.32 ± 0.04	0.3*	1.06	0.29 ± 0.01 [8]
CRM BCR 063a Skim Milk Powder	7	0.76 ± 0.07	0.81 ± 0.1	0.94	-
NIST SRM 1573a Tomato Leaves	7	0.77 ± 0.09	0.85*	0.91	-

Note : *Non certified value, **Ratio the experimental result to certificate value.

Table 5. Chlorine content of Biological Reference Material determined using ENAA at 5 MW with Cd foil as filter

SRM/CRM	N	Concentration in mg/kg			
		This work	Certificate	Ratio**	Literature
NIST SRM 1548a Typical Diet	7	12900 ± 600	12078 ± 356	1.06	12045 ± 382[13]
NIST SRM 1515 Apple Leaves	7	596 ± 50	579 ± 23	1.02	-
CRM BCR 063a Skim Milk Powder	7	9520 ± 475	9940 ± 356	0.96	-
NIST SRM 1573a Tomato Leaves	7	6610 ± 460	6600*	1.00	-

Note : *Non certified value, **Ratio the experimental result to certificate value.

Table 6. Bromine content of Biological Reference Material determined using ENAA at 5 MW with Cd foil as filter

SRM/CRM	N	Concentration in mg/kg			
		This work	Certificate	Ratio**	Literature
NIST SRM 1548a Typical Diet	7	8.21 ± 0.70	9.64*	0.85	10.07 ± 1.1[13]
NIST SRM 1515 Apple Leaves	7	-	-	-	-
CRM BCR 063a Skim Milk Powder	7	-	-	-	-
NIST SRM 1753a Tomato Leaves	7	1175 ± 60	1300*	0.90	-

Note : *Non certified value, **Ratio the experimental result to certificate value.

Table 4 to Table 6 are the analytical result of I, Br and Cl on biological standard reference material taken from NIST and BCR. The elemental concentration is presented as mean of N replicate of analysis. R is defined as ratio of the analytical result to the value of a given certificate. R was used to determine the proximity of the value of the certificate.

Overall, the analytical results show that the obtained R are close to one. Iodine and Chlorine have R-value of 0.91 to 1.06; meanwhile R for Bromine is 0.85 to 0.90.For the certified value, the analysis results obtained have fairly high compliance to the value of the certificate. Our result is close to the certificate value given, but with uncertainty relatively slightly higher than that on the certificate.

CONCLUSION

Utilization of Cd foil at EINAA to filter thermal neutron could reduce the Compton background until 10 times lower. Iodine, Chlorine and Bromine at biological sample could be determine quantitatively using Epithermal INAA. The analytical result of I, Cl and Bris close to the certified value with range ratio R of 0.85 to 1.06.

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