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Determination of selenium in biological materials by short-time neutron activation analysis using ^{77m}Se at the Dalat research reactor

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Abstract: A rapid neutron activation analysis technique for determination of the concentration of selenium in biological materials using short-lived radionuclide ^{77m}Se (half-life = 17.4 seconds) has been developed at Dalat Nuclear Research Institute (DNRI). The technique is very simple and rapid. It involves irradiation of a sample for 20 s, decay for 20 s and counting for 20 s. The accuracy of the method has been evaluated by analyzing a number of biological standard reference materials of varied selenium levels. An agreement between measured and certified values was acceptable in regarding to the deviation of the above mentioned two values within 8 percent. The result shows that the utilization of short-lived radionuclide ^{77m}Se is more useful in comparison with long-lived radionuclide ^{75}Se (half-life = 120 days). In addition, it is suggested that a further study for cyclic irradiations should be done in order to enhance the detection limit of the determination of the short-lived radionuclide ^{77m}Se.

Keywords: *Neutron activation analysis, short-lived radionuclides, selenium.*

I. INTRODUCTION

Selenium (Se) is considered an essential trace element. The discovery of Se as an essential element for animals was first reported in 1957. Since then, the Se requirement in humans has been evaluated and further knowledge has been acquired on its nutritional role [1, 2]. Selenium is widely distributed in the environment (waters, soil, air and biological materials) albeit generally in very low concentrations (≤ 1 mg/kg) [3, 4]. Selenium and its compounds have found in a broad range of technological applications, especially in pharmaceutics (veterinary selenium preparations in treatment of diseases due to selenium deficiency) [3]. Selenium is now better recognized as a biologically important nutrient. Insufficient dietary intake for satisfying biological requirements in several physiological or pathological conditions has been demonstrated, and it now establishes that inadequate intake has adverse consequences for disease susceptibility and the maintenance of optimal health [2].

A variety of analytical methods can be applied for the determination of trace amounts of selenium (µg/kg) in various materials. They include mainly: neutron activation analysis (NAA), atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), Gas-Liquid Chromatography (GLC), spectrofluorometry, x-ray fluorescence analysis and others [3]. NAA, AAS and spectrofluorometry are the most frequently used analytical techniques for the determination of selenium in biological materials [3-7]. The spectrofluorometry

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method is considered time-consuming and cumbersome, and the AAS method can suffer from matrix interferences, if appropriate precautions are not taken, when applied to such complex matrices as foods [5]. Moreover, selenium is often present in both environmental and biological samples in very low concentrations; highly sensitive analytical techniques are needed to prevent loss from volatilization or contamination. The NAA method offers high sensitivity by using either the long-lived radionuclide ^{75}Se (half-life = 120 d) or short-lived radionuclide ^{77m}Se (half-life = 17.4 s). Both methods have advantages and disadvantages. The determination of Se via ^{75}Se is a feasible method, but it takes a relative long analytical time and thereby increasing the analytical expense. The utilization of ^{77m}Se can be avoided lengthy irradiation, decay and counting periods of conventional NAA, thus allowing a significant reduction in total experiment time.

The nuclear data for the determination of Se by INAA are shown in Table 1. Selenium has six stable isotopes, which can produce seven radionuclides on thermal and epithermal/ fast-neutron activation. For the determination of selenium by NAA, the most commonly used radionuclide is ^{75}Se, which has a relatively long half-life of 120 d. The target isotope ^{74}Se has a low abundance of only 0.87%, but it is compensated by a fairly high epithermal and thermal neutron absorption cross-sections of 424 barn and 51.8 barn, respectively [7]. The utilization of the radionuclide ^{75}Se requires lengthy irradiation at a high neutron flux and long decay and counting times to achieve an acceptable sensitivity. The total experimental time is typically 2-3 week, which is time-consuming and expensive for the analysis of a large number of samples. Another drawback to the use of ^{75}Se is potential interferences resulting from overlapping gamma rays from other radionuclides (Table 1).

Alternatively, the short-lived radionuclide ^{77m}Se (half-life = 17.4 s) can be used for Se determinations [3-5, 8-10]. It can be produced by thermal and/or epithermal neutron absorption from isotope ^{76}Se, which has a 10 times greater isotopic abundance but lower cross-section than ^{74}Se, for both thermal and epithermal neutrons (Table I). Because the half-life of ^{77m}Se is very short, saturation activity can be reached in a short time, leading to enhanced sensitivity. The 161.9 keV γ-ray of ^{77m}Se could be interfered with the 162.3-keV γ-ray of ^{116m2}In with a half-life of only 2.18 s. However, a decay time of 20 s can eliminate this potential interference. Also, Indium is rarely detected in biological materials such as foods and diets and did not pose any problems in this study.

Table I: Nuclear data and interfering nuclides for selenium by INAA [2]

Nuclear data for selenium				**Interfering nuclides**	
Isotope (% abund.)	**σ_{th} (b)*; I_{epi} (b)***	**Nuclide; ($T_{1/2}$)**	**γ-ray (keV)**	**Nuclide ($T_{1/2}$)**	**γ-ray (keV)**
^{74}Se (0.87)	51.8 ± 1.2; 424 ± 17	^{75}Se; (119.8 d)	121.1 136.0 264.7 279.5	^{152}Eu ^{181}Hf ^{182}Ta ^{203}Hg	121.8 136.3 264.1 279.1
^{76}Se (9.02)	21 ± 1; 16 ± 0.2	^{77m}Se; (17.4 s)	161.9	^{116m}In (2.18 s)	162.3

σ_{th} , and I_{epi} is thermal and epithermal absorption cross section in barn (b) unit.

The first objective of this work was to determine analytical sensitivities and detection limits of selenium in biological materials by INAA method using short-lived radionuclide ^{77m}Se. The second was to evaluate analytical precision and accuracy of the method. The third was to show a comparison of two methods of determining selenium in biological materials by INAA using ^{77m}Se and INAA using ^{75}Se.

II. EXPERIMENT

A. Irradiation and counting system

The research was carried out by using fast pneumatic transfer system (PTS). The PTS has been installed at Dalat reactor for rapid INAA. This system can be used to perform short irradiations in seconds in either the vertical channel No.13-2 or the horizontal thermal column of Dalat reactor. The transfer time of sample from irradiation position to measurement position is approximately 3.2 seconds (including both transferring time of sample from irradiation position to detector and the time required to start the detector). The digital signal processing spectrometer has been installed in compacting with the PTS for measurement of sample's activity. It is connected to a 40% relative efficiency HPGe detector (GMX40-76-PL) coupled with a transistor reset preamplifier. It is selected and tuned for accurate measurement at high and varying counting rates, using loss-free counting technology [11]. Characterizations of this PTS has been reported elsewhere and thus will not be described here [12].

B. Sample preparation

Standards: All selenium standard solutions used in this work were made from Merck Millipore. These standards had a certified purity of > 99.999% and most of them had a concentration of 1000 mg/ L. A solution of a desired concentration was prepared by diluting from the 1000 mg/L standard dilution. Each 10 µg standard solution was pipetted on finely ground paper put in a 1.2-mL polyethylene vial and then dried under a ventilated box before sealing a cap.

Biological standard reference materials (Bio-SRMs): A number of SRMs used in this work are Tuna Fish IAEA-436, Oyster tissue NIST-1566b, Bovine Liver NIST-1577a and Bovine Liver NIST-1577. These Bio-SRMs were obtained from International Atomic Energy Agency (IAEA) and the US National Institute of Standards and Technology (NIST). These were used for quality assessment of INAA the method. All of SRMs were heated at 45^{0}C for 48 h to remove moisture. For each of these materials, approximately 200 mg was weighed and packed in a high purity polyethylene vial. Eleven sample replicates (IAEA-436, NIST-1566b) and four sample replicates (NIST-1577 and NIST-1577b) were prepared for each material.

C. Activation and measurement

All of the samples were activated at irradiation position of the No.13-2 channel of Dalat reactor and counted on a digital signal processing spectrometer connected to the fast pneumatic transfer system. At irradiation position of No.13-2 channel, the thermal neutron flux is 4.2×10^{12} neutron.cm^{-2}.s^{-1} and the epithermal neutron flux is $\sim 4 \times 10^{11}$ neutron.cm^{-2}.s^{-1} when the reactor is operated at power of 500 kW. Sample position is fixed at a distance of 10 cm away from detector surface.

To assess analytical sensitivities (counts/ s/ µg), selenium standard solutions were activated for 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60 s, respectively. After a delay of 3.2 s, each sample was measured for 20 s. In order to optimize irradiation time for the determination of Se in biological materials,

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two 200 mg replicates of each material (IAEA-436 and NIST-1566b) were irradiated for 5, 10, 15, 20, 25, 30, 35 and 40 s. After a delay of 3.2 s, each sample was measured for 20 s. Therefore, the optimal irradiation time is found at lowest detection limit. Thus, a number of Bio-SRMs (IAEA-436, NIST-1566b, NIST-1577a and NIST-1577) were analyzed for Se to test the precision and accuracy of the method. Each sample were activated for the optimal time that were found in the above experiment, then allowed 20 s delay time to eliminate interference of ^{116m}In with a half-life of 2.18 s [2, 5] and measured for 20 s (~ 1 $T_{1/2}$ of ^{77m}Se).

D. Calculation of detection limit and concentration of selenium

The detection limit for Se, LOD, is defined as the level at which a signal might be detected. At a 95% confidence level, a signal is said to be detected above the background signal (B), the interfering radionuclides, if LOD > ~3√B. Therefore, the concentration at which an element becomes detectable is expressed as sensitivity = 3√B/(P/m) (μg) according to Hou [13], in which P is the net area counts of 161.9 keV peak of the ^{77m}Se and m is the mass of selenium. The detection limits for Se could be high in the samples with the presence of large amounts of Al, Na, Cl and Br.

All Bio-SRMs are activated and measured in the same irradiation conditions and geometrical configuration of measurement. The concentration of the selenium (ρ_A) in the sample can then be derived from the result for the standard sample at the same gamma energy: $\rho_A = (P_A/ M_A/ D_A) / (P_S/ m_S/ D_S)$; in which P_A is the net counts of 161.9 keV peak of the ^{77m}Se in the analysis sample, P_S is the net counts from the same gamma peak in the standard sample, M_A and m_S are the mass of sample and the mass of selenium in standard (g), respectively. D_A and D_S are the decay correction of element of interest in the sample and standard, respectively [14].

III. RESULTS AND DISSCUSION

Experimental measurement of analytical sensitivities was made for selenium by using selenium standard solution. The results for these measurements are found in Fig 1. The data obtained confirm that irradiation for above 5 s at irradiation position in the No.13-2 channel (the thermal flux of 4.2 x 10^{12} neutron/cm^2/s^1) coupled with measurement of roughly 20s and at 10 cm approximately away from detector will provide adequate analytical sensitivities for rapid determination of selenium.

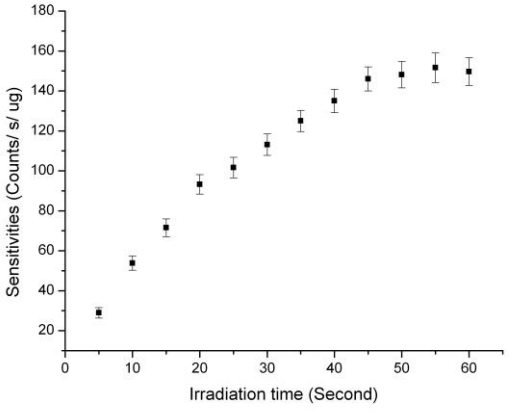

Fig.1. Results from the measured sensitivities of Se in the selenium solution standard with various irradiation times

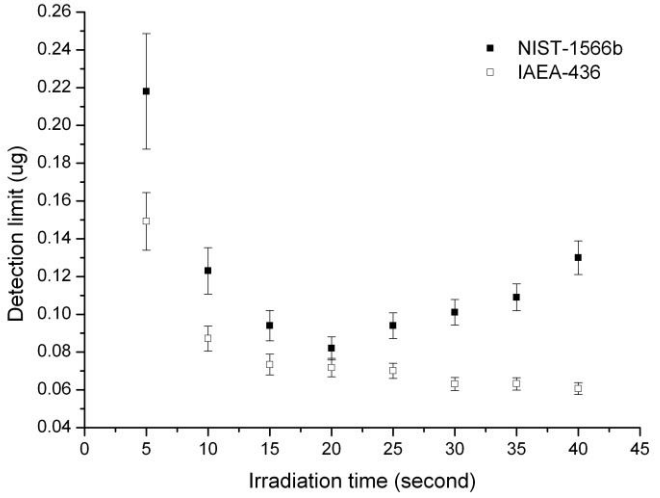

Fig. 2. The detection limits of Se in IAEA-436 and NIST-1566b with various irradiation times

Measurements of detection limits of Se in IAEA-436 and NIST-1566b with various irradiation times were performed. The results for these measurements are presented in Fig 2. The results show that for irradiation time of 15 ÷ 30 s, at irradiation position of the No.13-2 channel coupled with measuring for roughly 20 s at approximately 10 cm away from detector, a detection limit of the range 0.06 ÷ 0.08 µg can be easily obtained for IAEA-436, whereas a detection limit of 0.08 ÷ 0.10 µg is more realistic for NIST-1566b which contain large amounts of salt (5140 ppm Cl and 3297 ppm Na) and Al (197.2 ppm).

The accuracy for the determination of selenium in the biological materials using the short-lived radionuclide ^{77m}Se was evaluated by analyzing a number of certified Bio-SRMs with different levels of Se. The average result of eleven analyses for IAEA-436 and NIST-1566b, and four analyses for NIST-1577 and NIST-1577a are shown in Table II. The agreement between measured and certified values was generally good with u-score < 1.64 in most cases. The precision of measurements is expressed in terms of relative standard deviation. The data indicate that the precision is ± 11% for determining selenium in IAEA-436 and NIST-1566b, ± 9% for determining selenium in NIST-1577, and ± 13% for determining selenium in NIST 1577a.

Table II. The results of concentration (in ppm) analysis for Se in biological SRMs.

Reference material	Certificated value	This work	u-score
Tuna Fish, IAEA-436	4.63 ± 0.48	4.25 ± 0.46	0.57
Oyster Tissue, NIST-1566b	2.06 ± 0.15	2.28 ± 0.24	0.78
Bovine Liver, NIST-1577	1.10 ± 0.10	1.16 ± 0.10	0.42
Bovine Liver, NIST1577a	0.73 ± 0.06	0.79 ± 0.10	0.51

For the determination of the selenium by NAA at DNRI, the long-lived radionuclide ^{75}Se or the short-lived radionuclide ^{77m}Se can be used [7]. With the short-lived radionuclide ^{77m}Se, not only completion times are a distinct advantage but also analytical sensitivities can be equal to NAA using the long-lived radionuclide ^{75}Se. The data for procedures are listed in Table III.

Table III. Experimental parameters were used for analysis of selenium in biological materials by NAA using ^{77m}Se and NAA using ^{75}Se isotopes at DNRI

Radionuclide	**^{75}Se**	**^{77m}Se**
Half-life	120 d	17.4 s
Activation	10 h at 3.5 x 10^{12} (n/cm^2/s)	20 s at 4.2 x 10^{12} (n/cm^2/s)
Decay time	20 d	20 s
Counting time	2÷3 h at GMX-30190	20 s at GMX-4076
Detection limit	0.06 ÷ 0.07 µg	0.06 ÷ 0.09 µg
Precision	8%	11%
*Accuracy	4.35 ± 1.1 µg/g	4.25 ± 0.46 µg/g

**The accuracy was tested by using the IAEA-436 with a selenium content Se of 4.63 ± 0.48 ppm*

IV. CONCLUSION

The neutron activation analysis method using short-lived radionuclide ^{77m}Se was developed at Dalat reactor for the determination of selenium in biological materials. It is very simple and rapid. The precision of measurement is typically ± 11%. The accuracy is well within ± 8% in most cases. Detection limits of 0.06 ÷ 0.09 µg can be easily achieved for a number of biological matrices. Detection limits are higher for the samples containing large amounts of Al, Na and Cl. Therefore, it is suggested that a further study for cyclic irradiations should be done in order to enhance the detection limit in the determination of the short-lived radionuclide ^{77m}Se.

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