

DETERMINATION OF SELENIUM IN ENVIRONMENTAL SAMPLE BY GAMMA-GAMMA COINCIDENCE METHOD

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Abstract: Selenium (Se) is considered an essential trace element, it plays a role in thyroid function and your immune system which needs Se to work properly. Se is widely distributed in the environment, so the quantifying Se in the environmental samples are very important and essential to study transferring factor. The advantage of coincidence method is abilities of background reduction and removal of interference evaluated for the analysis of geological samples [1]. In this paper, we would like to present determination of the results of Se in environmental sample by neutron activation analysis combined with the gamma-gamma coincidence method. By application of this method, the peak to background ratios, detection limits of Se in environmental samples were improved and concentration of Se in sample was determined.

Keywords: Neutron activation analysis, gamma-gamma coincidence, Determination of Se, Environmental samples.

1. Introduction

The gamma-gamma coincidence method is mainly applied for experimental studies of the nuclear structure. Thanks to its ability to reduce the gamma rays background and the selection of events correlation in timing, these methods have been used for NAA [2- 5]. Lawrence E. Wangen et al have used a coincidence method using Ge(Li) Detectors to evaluate Se detection limits and background reductions for Normal and Coincidence counting procedures [2].

Y. Hatsukawa et al have used a coincidence spectroscopy with detector arrays in order to improve sensitivity of NAA. In this manner, 24 elements in the reference igneous rock samples were determined simultaneously without chemical separation [4].

When determination of Se in the Bovine Liver SRM-1577 sample by the Instrumental neutron activation analysis (INAA) method, B.E. Tomlin et al have improved the peak to background ratios at 121.1 keV, 136.0 keV, 264.7 keV and 279.5 keV of ⁷⁵Se to 257.1, 360.0, 733.1 and 598.6 respectively when comparing coincidence and normal measurement [5].

Determination of Se in environmental samples, geological samples and biological samples by the INAA method, the isotope of choice is ⁷⁵Se and its gamma lines situated at 121.1 keV; 136.0 keV; 264.7 keV; 279.5 keV and 400.7 keV. These gamma rays are influenced by gamma rays of isotopes as ¹⁵²Eu (121.8 keV), ¹⁸²Ta (264.1 keV), ²⁰³Hg (279.2 keV), ¹⁸¹Hf (136.3 keV) and ²³³Pa (398.5 keV). So that, the determination of low concentrations of selenium in environmental samples is a difficult analytical problem.

Recently, the gamma-gamma coincidence methods have been shown to give accurate determination of Se in geological sample in Dalat Nuclear Research Reactor [1], and the interference of other gamma rays at the energy of interest such as the ¹⁵²Eu, ¹⁸¹Hf and ¹⁸²Ta lines which interfere with the detection of ⁷⁵Se were solved without the need for radiochemical separation. This work, we applied processes the same described in Reference [1], in order to [7] determine Se in environmental sample by gamma – gamma coincidence method.

2. Experimental

2.1. Sample preparation

The testing sample was prepared from a standard material of Coal Fly Ash-1633b [6]; 131.1mg sample was sealed in a high purity polyethylene bag and irradiated at central irradiation tube with neutron flux $\sim 3.4 \times 10^{13} \text{ n.cm}^{-2}.\text{s}^{-1}$ for 10 hours. After 60 days decay time, the sample was counted on the gamma-gamma coincidence spectrometer in normal mode and coincidence mode. The electronics configuration of gamma-gamma coincidence spectrometer is shown in figure 1.

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2.2. Measurement

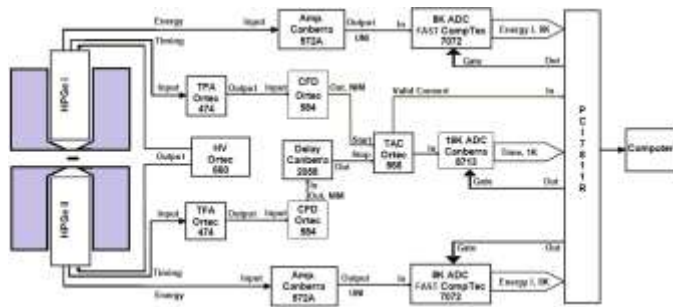


Fig. 1. The experiment arrangement and electronics configuration

The coincidence spectrometer includes two HPGe detector, type GMX35 of 35% and 38% relative efficiency, and 1.9 keV energy resolution at 1332 keV of a ⁶⁰Co source.

The sample was centered on the axis of the two detectors at a distance of 4 cm between the sample and the end cap of each detector. The parameters of spectroscopy are setup by method described in Reference [6]. In the normal mode, the spectra were acquired for 0.8 hours and in gamma-gamma coincidence mode, for 48 hours. The collected data were saved and analyzed off-line by multi-parameters method.

2.3. Data analysis

In the normal mode spectroscopy, the peak area were measured by fitting with colegram software [6], and corrected by comparing with certified standard sample. The 482.2 keV peak area of ¹⁸¹Hf was used to assess the contribution of this isotope in the peak 136.3 keV; and the peak 1221.4 keV of ¹⁸²Ta was used to assess the contribution of this isotope in the peak 264.1 keV.

In the gamma-gamma coincidence mode, the gamma rays emitted form trace elements were analyzed using gated spectra obtained by putting gates on γ - γ matrix. The double fold γ - γ coincidence events were stored to a two-dimensional E_γ - E_γ matrix, which had 2048-channel \times 2048-channel size. A gate spectrum was obtained, by gating on a γ -ray energy in one detector, from a second detector in coincidence with the first one. In order to correct for the chance coincidence in the gate spectrum, the spectrum gated at background region near the peak position was subtracted from the spectrum at the peak. A typical gated spectrum for 136.0 keV and 264.7 keV are shown in Fig. 2. The detection limits were evaluated, assuming a γ -peak area was twice the standard deviation of the underlying background. The detection limits (for normal or coincidence mode) were calculated as follows Eq. 1 [9]:

$$C_{DL} = \frac{3.29C \sqrt{1 + \frac{\eta_p}{\eta_B}}}{\sqrt{\left(\frac{P}{B}\right)\left(\frac{P}{t}\right)}} \quad (1)$$

where:

P/B is the peak-to-background ratio;

P/t is the net counting rate in the peak;

t is the counting time;

C_{DL} is the detection limit in units of concentration;

C is the concentration or activity;

η_p and η_B are standard deviations of peak and background.

The concentration of Se in the sample (for normal or coincidence mode) were calculated as follows Equation 2 [10]:

$$\rho = \frac{\left(\frac{N_p / t_c}{W.D.C}\right)_a}{\left(\frac{N_p / t_c}{W.\rho.D.C}\right)_s} \quad (2)$$

Where:

N_p is the net area of the sample (a) and standard (s)

$S = 1 - \exp(-\lambda t_i)$ is the saturation factor, t_i is the irradiation time;

$D = \exp(-\lambda t_d)$ is the factor decay time, t_d is the decay time;

$C = [1 - \exp(-\lambda t_c)] / (\lambda t_c)$ is the factor counting times, t_c is the counting times;

W is the weight of the sample and standard (g);

ρ is the concentration of the element (mg/kg).

The ⁷⁵Se isotope has gamma cascade rays at 121.1-279.5 keV and 136.0 - 264.7 keV. In this cascade, the pairs of 136.0 - 264.7 keV present the strongest intensities. The coincidence gating will remove both the ¹⁸²Ta interference at 264.1 keV and ¹⁸¹Hf interference at 136.3 keV. The lower intensity 400.7 keV γ ray was not use at all. The instrumental removal of these interfering gamma rays avoids the need of complex chemical separation, and should be considered as the method of choice, especially when Hf and Ta concentrations are large compared to the Se concentration.

3. Results and discussions

3.1. Results

The gate spectra corresponds peak 136.0 keV and peak 264.7 keV were shown in figure 2 for which the contributions of interferences are evaluated. Figure 3 and 4 show the extended spectra in coincidence and in normal mode for the Coal Fly Ash-1633b sample highlighting ⁷⁵Se main gamma lines. The peak to background ratios, detection limits and concentration of Se, which are gating of corresponding gamma energies, are shown in the table 1 and table 2.

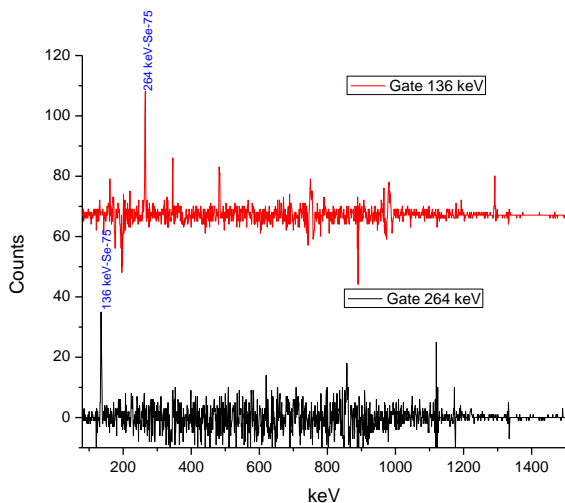


Fig. 2. The gate spectra with energy gamma rays of 136.0 keV and 264.7 keV of Coal Fly Ash in energy region from 0-1500 keV.

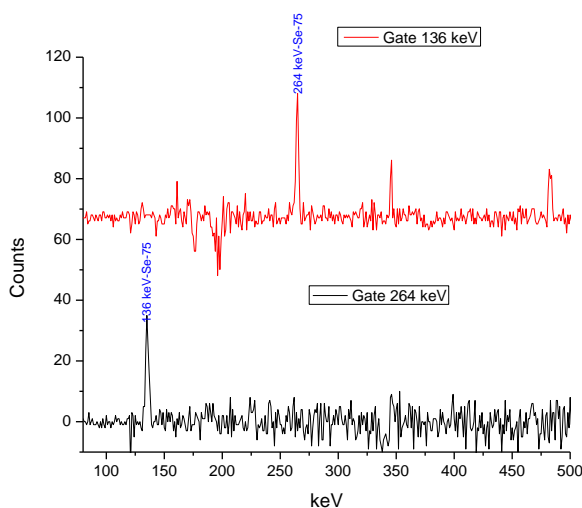


Fig. 3. The gate spectra with energy gamma rays of 136.0 keV and 264.7 keV of Coal Fly Ash in energy region from 100-500 keV.

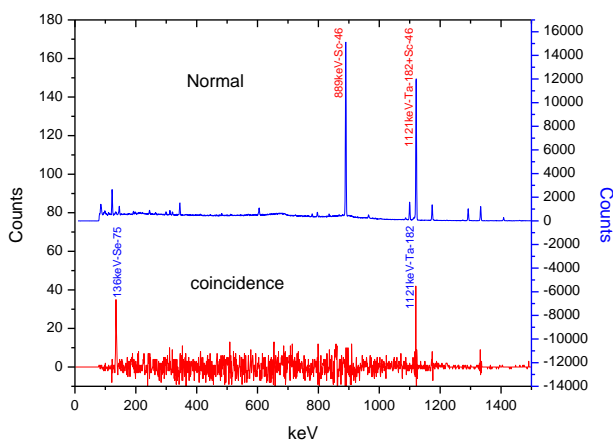


Fig. 4. The spectra of Coal Fly Ash in normal and coincidence modes; the coincidence is gated at 264.7 keV.

Table 1. The peak to background ratios, detection limits and Concentration of selenium in Coal Fly Ash in normal and coincidence modes.

Energy (keV)	Peak to background ratios		Detection limit (mg/kg)	
	Normal	Coincidence	Normal	Coincidence
136 (keV)	0.09	7.67	0.30	0.07

Table 2. The Concentration of selenium in Coal Fly Ash in normal and coincidence modes.

Energy (keV)	Concentration (mg/kg)		Concentration (mg/kg)
	Normal	Coincidence	Certificate
136 (keV)	9.78 ± 0.59	10.01 ± 0.30	10.26 ± 0.17

3.2. Discussions

Based on figure 2, the inferences of the isotopes ¹⁸²Ta and ¹⁸¹Hf were evaluated. In our previous articles we were introduced [1], use peak 264 keV for gating is good. because the statistics of peak 136 keV in the spectrum were better but the 136 keV is near the 133 keV gamma ray of ¹⁸¹Hf so the determination of background is more difficult than using 264 keV for gating.

Result in tale 3 showed that the gamma-gamma coincidence method, application for activation Se in environmental sample. The inferences of the isotopes were evaluated as in geological sample, but detection limit is better because the environmental sample has concentration of Se more than geological sample.

The detection limit in coincidence mode is improved about 4.56 times and the peak to background ratios is improved about 87.33 times. In the case of using 264 keV for gating, the interference of other isotopes was nearly solved.

4. Conclusion

The gamma-gamma coincidence method have been shown to give accurate determination of selenium in environmental sample. The advantages of this method are low detection limit, the interference of other gamma rays at the energy of interest such as the ¹⁸¹Hf and ¹⁸²Ta lines which interfere with the detection of ⁷⁵Se were solved without the need for radiochemical separation.

This study has improved detection limit and peak to background ratios and determined concentration of Se in environmental sample with accuracy of concentration and errors is better.

The main disadvantage is the low sample throughput of about one sample a day, using the procedure presented here.

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