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Determination of Arsenic with Overlap Peaks in Neutron Activation Analysis by Event-Event Coincidence Technique

TRUONG VAN MINH[1], NGUYEN XUAN HAI[2,*], NGUYEN NGOC ANH[2], PHAM DINH KHANG[2] and HO HUU THANG[2]

[1]Department of Natural Sciences, Dong Nai University, Dong Nai, Vietnam
[2]Dalat Nuclear Research Institute, Dalat, Vietnam

*Corresponding author: Tel: +84 0919 979 673; E-mail: nxhai@hcm.vnn.vn; xuannguyennri@gmail.com

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The high compton background and peak overlap restrict the applicability of instrumental neutron activation analysis (INAA). The coincidence technique can greatly reduce these problems. Some previous results have proved the ability of event-event coincidence method for determination of elements with overlap peaks in complex matrix sample. In this work, we analyzed arsenic in geological sample to evaluate advantages of the coincidence technique in instrumental neutron activation analysis. An innovation in data analysis process, which helps to reduce the measurement time and to improve the detection limit is also presented.

Keywords: Event-event coincidence, Neutron activation analysis, Detection limits.

INTRODUCTION

An ability to reduce the gamma background and to select the useful analysis, the gamma-gamma coincidence method has been used for both INAA and prompt gamma neutron activation analysis (PGNAA) [1-4]. Normally, due to complex background matrix of the sample, the gamma spectrum in conventional INAA method is very complicated. First, characteristic peaks of the interested elements are usually superimposed on a high continuous Compton background caused by high-energy γ-rays of Na, K and Br in the sample itself or in the surrounding material of the detector. Secondly, peaks of some special elements, such as Se and As, in environmental, biological or geological sample may be overlapped with one of ^{152}Eu, ^{182}Ta, ^{181}Hf. Because of these problems, the determination of such elements like Se and As in geological sample becomes very difficult in some cases. Fortunately, those difficulties can be remarkably brought down by gamma-gamma coincidence method.

In Dalat Nuclear Research Reactor (DNRR), a gamma-gamma coincidence spectrometer has been setup for neutron activation analysis and experimental studies of nuclear structure [5]. This spectrometer was used to determine selenium in geological sample [6] and environmental sample [7]. The accuracy of the method was confirmed and the detection limit was less than 1 mg/kg in both cases. The overlap of ^{75}Se characteristic peaks with one of ^{181}Hf and ^{182}Ta was successfully treated without the need of radiochemical separation process. In comparison with conventional INAA method, the coincidence method considerably improved the peak to background ratio and the detection limit, approximately 167 and 2.87 times, respectively for geological sample [6], then 87.33 and 4.56 times for environmental sample [7]. An innovation in data analysis process to ameliorate the lack of collected data in coincidence method due to measurement time limitation was also introduced.

In this work, we analyzed the presence of arsenic in geological sample that has more complexity of background matrix. Based on the result, we evaluate the ability of event-event coincidence method in INAA in determination of selenium.

EXPERIMENTAL

Sample preparation: The used standard samples were prepared from Merck Millipore produced arsenic standard solutions. The standard solution had certified purity of more than 99.999 % and concentration of 1 mg/L. A standard sample of desired concentration was prepared from the standard solution by dilution. The standard solution was first pored over a ground paper, which was put in a 1.2 mL polyethylene vial, by using a pipette. The combination was then dried in a ventilated box and finally was sealed. Four standard samples, which correspond with arsenic weights of 0.5, 5, 15 and 20 μg, were prepared and were irradiated in DNRR under the same conditions, as geological sample was.

Geological sample: The testing geological sample was prepared from a standard material of Montana II Soil SRM–2711a [8]. The sample, which weighed 52.1 mg, was covered by a high purity polyethylene bag and was irradiated for 10 h at the central irradiation tube of DNRR. The *in situ* neutron flux was approximately 3.4×10^{13} n cm^{-2} s^{-1}.The sample decay time was 90 h.

All measurements were performed with the event-event coincidence gamma spectrometer [5], which could operate in two modes: normal mode and coincidence mode. The two used detectors were Ortec HPGe type GMX35 of 35 % and 38 % relative efficiency and 1.9 keV energy resolutions at 1332 keV of ^{60}Co source. The electronics configuration of spectrometer is shown in Fig. 1.

In normal mode, the spectrometer functioned as a simple traditional gamma spectrometer using only one HPGe detector, which collected data in form of spectrum. In coincidence mode, two detectors were used and data were collected in form of discrete digital values in proportion to absorbed gamma energies of two detectors.

Two detectors were placed coaxial and opposite to each other. The distance between two detector windows was 8 cm and the samples were put at the center. Each sample was measured for 4.5 h in normal mode and 46 h in coincidence mode.

Data analysis: In normal mode, the area of the peak corresponding to 559 keV line of ^{76}As (45 % absolute intensity) was used to determine the concentration of arsenic in the sample. The detector energy resolution was only 1.9 keV, thus the 559 keV peak was overlapped with 563 keV peak and 564 keV peak that correspond with 563 keV line of ^{76}As (1.2 % absolute intensity) and 564 keV line of ^{122}Sb (70.5 % absolute intensity), respectively. To solve the problem of peak overlap, Fitz Peak Gamma Analysis software was used to determine 559 keV peak area through a deconvolution procedure.

For coincidence analysis, we set two gates, one on 559 keV line and one on 657 keV line. Based on the decay scheme of ^{76}As, these are two strongest transitions, which are in cascade with many other γ-rays. Owing to the difference of the linearity between two used ADCs, the energy/channel ratio of two detectors were not the same. A shifting process was carried out to calibrate values of event-event. The difference of energy/channel ratios was small enough; hence, the shifting process did not cause spectrum distortion. A gated spectrum was obtained, by selecting the events from a detector coincidence with events, which correspond to a determined γ-peaks from the another detector. Therefore, each detector provided a gated spectrum. By using shifting process, we could add the two-gated spectra into one. In order to correct for the random coincidence in the gate spectrum, the spectrum gated at background region near the peak position was subtracted from the spectrum at the peak.

The detection limits were evaluated, assuming a gamma-peak area was twice the standard deviation of the underlying background. The detection limits (for both normal and coincidence mode) were calculated as follows eqn. 1 [9].

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

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.

RESULTS AND DISCUSSION

Table-1 shows count rates of 559 keV line and 657 keV line corresponding to various standard samples, which had different concentrations, in coincidence mode.

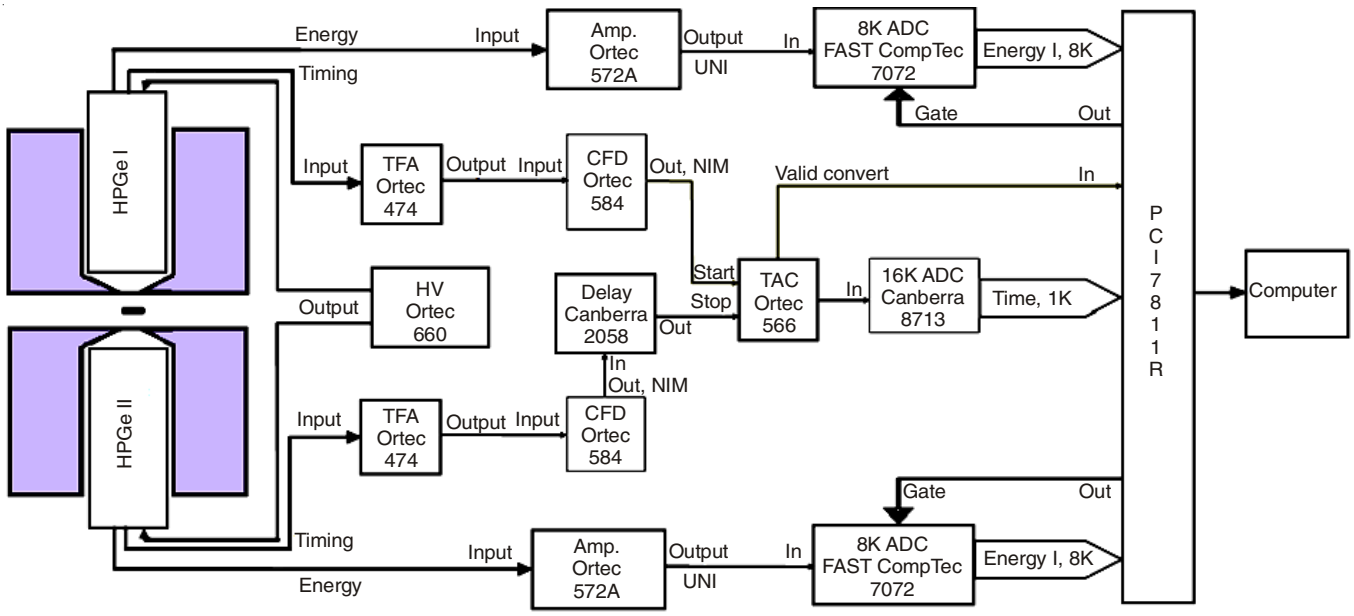

Fig. 1. Experimental arrangement and electronics configuration

TABLE-1
COUNT RATE OF 559 keV PEAK AND 657 keV PEAK (cps) CORRESPONDING TO SAMPLES OF VARIOUS CONCENTRATIONS (ppm)

Concentration (ppm)	559 keV (cps)	657 keV (cps)
0.5	0.58 ± 0.001	0.51 ± 0.004
5.0	5.47 ± 0.006	4.90 ± 0.016
15.0	20.30 ± 0.020	18.10 ± 0.054
20.0	25.60 ± 0.027	22.90 ± 0.071

A good linearity between count rates and concentrations of standard samples that shows in Fig. 2 confirms the ability of applying coincidence method in INAA. The goodness of fits is demonstrated by adjusted coefficient of determination (R-Square), which are 0.9943 in case of 559 keV line and 0.9948 in case of 657 keV line. The shifting process helps us to use gated data from both detectors, therefore increasing statistic about two times without increasing measurement time. While long measurement time is still an unsolved disadvantage of coincidence method, our small innovation in data analysis partially reduces this problem.

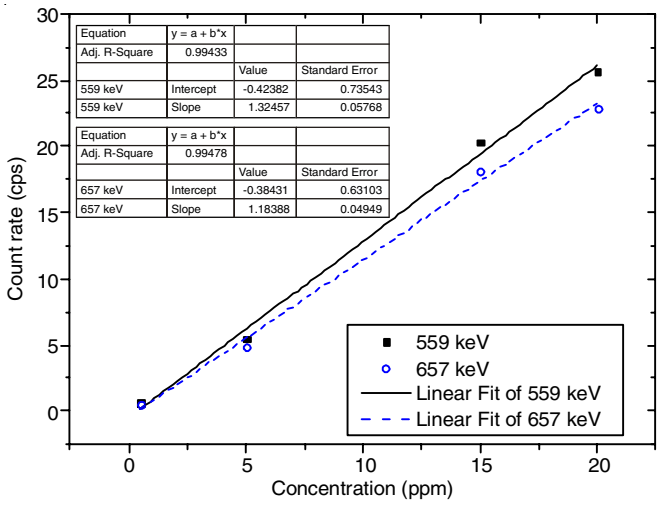

Fig. 2. Relationship between count rate and concentration

Fig. 3 shows that 559 keV gated spectrum is more complex than the 657 keV one. In the 657 keV gated spectrum, only 559 keV peak appears, compared to three in 559 keV gated spectrum. Thus, the 657 keV gated spectrum was chosen to compare with the normal spectrum (Fig. 4). While the 559 keV line is overlapped with 563 keV and 564 keV lines in normal spectrum, it appears as a single peak in 657 keV gated spectrum. In evidence, the peak overlap was successfully solved by coincidence method. Although a deconvolution process can also mathematically solve the peak overlap, its confidence is always in question. Combining deconvolution process with stripping method can give us a better way to handle peak overlap, but it requires some knowledge of sample compositions that we do not usually have.

Both peaks to background ratio and detection limit in coincidence mode are improved 8.6 and 4.16 times, respectively in comparison with normal method. The background matrix of arsenic sample is complex, however the results in Table-2 showed that coincidence method can obviously solve the difficulty. Thus, the coincidence method can well support

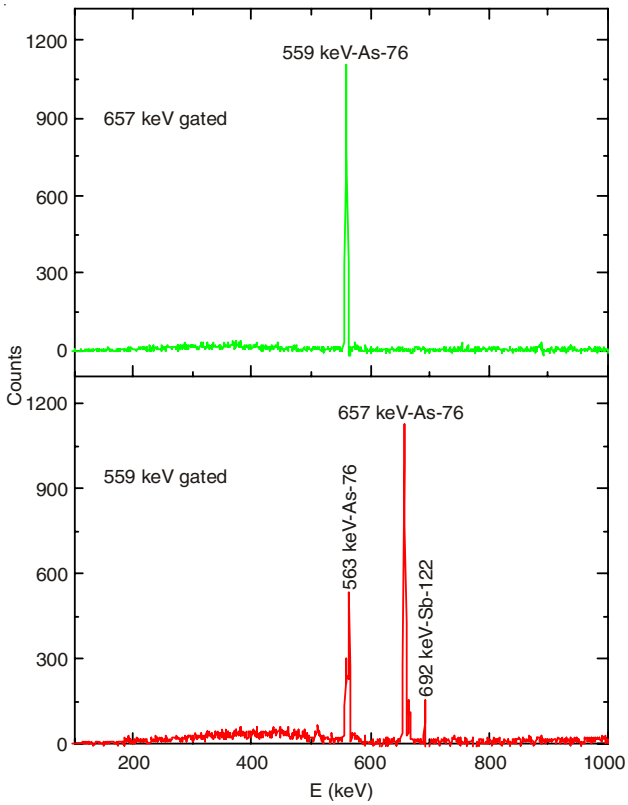

Fig. 3. Gate spectra with 559 keV and 657 keV lines

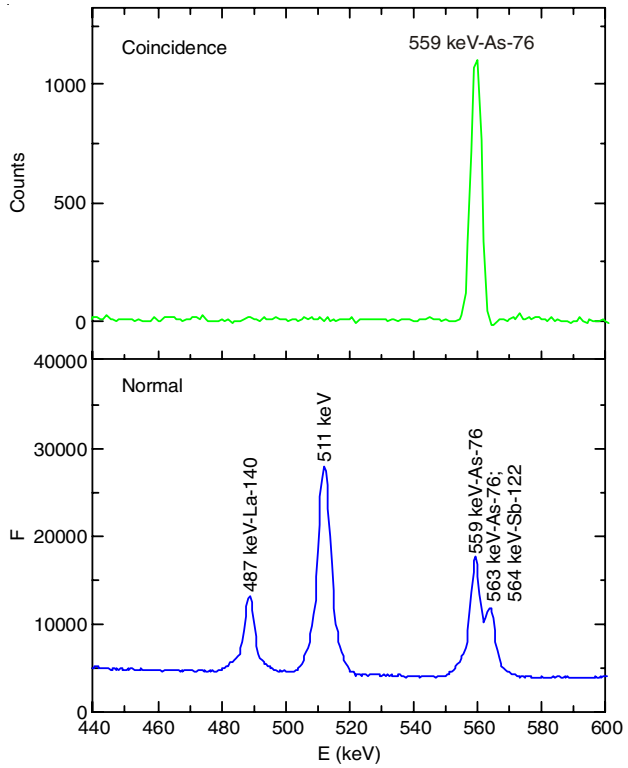

Fig. 4. A part of coincidence gated spectrum and normal spectrum; 559 keV peak appears in gated spectrum as a single peak, but is overlapped with 563 keV and 564 keV peaks in normal spectrum

to conventional INAA in general and even replace it in some particular cases, such as arsenic determination in present work or selenium determination in our previous publications [6,7].

TABLE-2
PEAK AREAS, THE PEAK TO BACKGROUND RATIOS, DETECTION LIMITS IN NORMAL AND COINCIDENCE MODES

Peak (keV)	Peak area (count)		Peak to background ratio		Detection limit (ppm)	
	Normal	Coincidence	Normal	Coincidence	Normal	Coincidence
559 keV (As-76)	66294	4455	0.77	6.62	0.79	0.19

Conclusion

The arsenic determination with overlap peaks in neutron activation analysis was solved by event-event coincidence technique. Due to some disadvantages, such as the quantity of isotopes that have appropriate nuclear structure for coincidence neutron activation analysis, long time measurement, complex spectrometer, the INAA method using coincidence technique has not replaced the traditional one. However, the coincidence technique plays an important role to improve the analysis quality and to enlarger the applicability of traditional INAA. In order to improve capability of event-event coincidence method, the improvement of efficient measurement is most important.

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