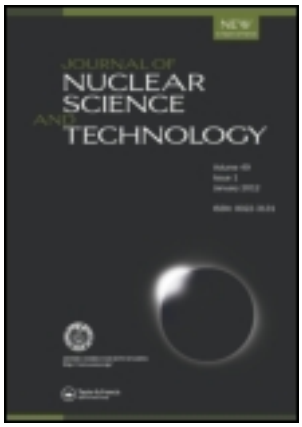

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A new trace-element quantification method has been developed by combining multiple gamma-ray detection and neutron activation analysis. This method is characterized by high sensitivity and simultaneous analysis for multi-elements. The quantification accuracy amounts to 3–20% depending on statistics. It has been successfully applied to the analyses of igneous rock samples, long-lived radionuclide, ^{129}I, and geologic samples. Future perspectives for an innovative pulsed neutron source and a new detector system will be presented.

KEYWORDS: neutron activation analysis, gamma-gamma coincidence, JRR-4 reactor, GEMINI, quantification accuracy, detection limit, iodine 129, iridium 192

I. Introduction

As an important application of radioisotopes, neutron activation analysis (NAA) is widely used in the fields of environmental science, biology, and astrophysics. Neutron activation analysis usually utilizes a single detector to measure gamma-rays from a neutron-activated sample. The energy resolution of a high-resolution germanium detector is approximately 1,000. However, since the number of gamma-rays from the sample with multiple elements often exceeds one thousand, it becomes impossible to resolve all of them. Weak gamma-rays, in particular, are masked by strong ones and their quantification is difficult. In order to circumvent this problem, we adopted multiple gamma-ray detection method to improve NAA.

II. NAA with Coincident Gamma-ray Detection

1. The Principle

We have developed a new method of trace element analysis based on neutron activation with coincident gamma-ray detection (NAACG). We took advantage of the fact that many radioactive nuclides emit multiple coincident gamma-rays. By detecting the coincident gamma-rays we can create a gamma-gamma two-dimensional matrix which incorporates the correlation among the gamma-rays. On this matrix we can achieve an energy resolution of 1,000,000, because the resolution reduces to the product of those in each axis. Since the number of gamma-rays produced in NAA does not exceed 10,000, one can separate completely as many nuclides as present in a sample (even if all the stable isotopes are present). We applied this technique to the neutron activation analysis.

2. Demonstration and the Result

To demonstrate the validity of this technique, we performed a test experiment for standard rock samples, JB-1a(basalt) and JP-1(peridot), issued by Japan Geological Survey. The weight was 100 mg each. The samples were irradiated with neutrons from the JRR-4 reactor at Japan Atomic Energy Research Institute (JAERI) with a flux of 3.3×10^{13}/s/cm^2. Gamma-rays were measured with a gamma-ray detector array, GEMINI, which comprises twelve BGO Compton suppressed germanium detectors.[1] The source-to-target distance is 13 cm and total solid angle is 7.4% of 4π. The detection efficiency of each Ge detector is 40–70% relative to a $3''\times3''$ NaI scintillator. The peak-to-total ratio is 0.50. The total detection efficiency amounts to 1.5%. Gamma-gamma coincidences were measured for 100 and 24 h for JB-1a and JP-1, respectively. The timing resolution was 50 ns. It turns out that 4 ppb of europium was successfully identified as the minimum quantity in those samples. Broad dynamic range from %(10^{-2}) to ppb(10^{-9}) order could be addressed in a single measurement. Since any destructive procedure such as chemical separation was not applied, volatile elements such as bromine were not lost in the whole procedure so that they are quantified accurately. For those samples totally 27 elements have been quantified and their minimum quantity was ppb(10^{-9}) order in europium.[2,3]

3. Quantification Accuracy Based on Comparison Method

Quantification is often made by the comparison method: a sample of interest and a standard sample including a known amount of any element are irradiated by neutrons at the same condition and their gamma-ray intensities are compared; The quantity of the element can be deduced from their ratio. This procedure does not include any nuclear data (except the half-life for the decay correction) and thus gives an accurate result. However, it has been applied only for single element so far. We have prepared two types of grand standard samples, which include 23 elements altogether with different quantities. The irradiation and measurement for both samples were made for 10 min and 24 h, respectively. With the coincident gamma-ray detection technique, the reproducibility of the weight from gamma-ray measurement has been tested. In this way, it has been proven that 23 elements can be quantified simultaneously with an accuracy of 3–20% depending on statistics.[4]

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4. Detection Limits

Table 1 shows a relative weight for each element required to get 20 counts in the gamma-gamma matrix for the grand standard sample. The relative weight is dependent on nuclear data of neutron cross section, decay lifetime and intensity of cascade gamma-rays. It also depends on instrumental conditions of the neutron flux, irradiation and measurement time, and detector efficiency. The relative weight is considered to reflect the sensitivity of each element. However, since the major component often limits total gamma-ray counting rate, there exists ambiguity on the detection limit. With the present detector system, the detection limit can be estimated as the following:

$$\text{Detection limit} = [\text{Relative weight}] \times 10^{-(2\text{-}4)},$$

where the factor depends on the major components in the sample.

5. Summarized Features of NAACG

By the gamma-gamma coincidence technique, we could achieve a high resolution of 1,000,000 ($E_\gamma/\delta E_\gamma$). This enables simultaneous quantification of 49 elements. (In **Table 2** we summarize the elements by the applicable analysis.) Because of this, there is no need for chemical separation. This is very important because we are free from the exposure to radiation. Also high precision is guaranteed without chemical yields (efficiency of chemical separation). The quantification accuracy amounts to 3% except statistical uncertainty. Since the background is mostly localized in a small region on the matrix, high sensitivity can be achieved, that is 10 fg from 10 mg sample (10^{-12} order).

We need to pay a price for these merits. While we need cascade gamma-rays, nuclides originating from 23 elements do not emit multiple gamma-rays; ordinary one-dimensional method needs to be applied for these elements. The other 12 elements are not suited for neutron activation analysis because they do not emit any gamma-ray or the decay lifetimes are too short.

Table 1 Relative weights to get 20 counts in the gamma-gamma matrix for grand standard sample

Element	Relative weight	Element	Relative weight
^{152m}Eu	1.8×10^{-9}	^{181}Hf	8.0×10^{-7}
^{192}Ir	7.0×10^{-8}	^{182}Ta	9.6×10^{-7}
^{177}Lu	4.0×10^{-8}	^{171}Er	5.4×10^{-7}
^{140}La	5.6×10^{-8}	^{60}Co	3.0×10^{-6}
^{153}Sm	5.2×10^{-8}	^{124}Sb	3.4×10^{-6}
^{160}Tb	7.2×10^{-7}	^{122}Sb	7.2×10^{-7}
^{46}Sc	1.2×10^{-7}	^{75}Se	2.6×10^{-6}
^{187}W	4.0×10^{-7}	^{143}Ce	2.8×10^{-5}
^{82}Br	7.8×10^{-8}	^{99}Mo	1.8×10^{-5}
^{76}As	2.4×10^{-7}	^{197}Hg	9.0×10^{-5}
^{198}Au	2.0×10^{-7}	^{131}Ba	2.4×10^{-4}
^{72}Ga	1.5×10^{-7}	^{110}Ag	2.6×10^{-5}
^{175}Yb	3.4×10^{-7}	^{114}In	1.1×10^{-4}
^{188}Re	2.6×10^{-7}	^{197}Pt	2.0×10^{-5}
^{169}Yb	3.4×10^{-6}	^{193}Os	2.0×10^{-5}
^{134}Cs	1.3×10^{-6}	^{77}Ge	1.4×10^{-4}

Table 2 Classification of elements by the applicable analysis

(a) 49 elements suitable to NAACG Detection limit 10^{-6}–10^{-12}
Ag, As, Ba, Br, Ca, Cd, Ce, Cl, Co, Cs, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, I, In, Ir, K, La, Lu, Mn, Mo, Na, Nd, Ne, Ni, Os, Pt, Ra, Rb, Re, Ru, Sb, Sc, Se, Sm, Sn, Ta, Tb, Th, Ti, U, W, Yb, Zn
(b) 23 elements only suitable to ordinary NAA (one-dimensional method) Detection limit 10^{-2}–10^{-6}
Al, Ar, Au, Cr, Cu, Dy, F, Ho, Kr, Mg, Nb, Pd, Pr, Rh, S, Sr, Te, Tl, Tm, V, Xe, Y, Zr
(c) 12 elements not suited to NAA
B, Be, Bi, C, H, He, Li, N, O, P, Pb, Si

6. On Line Analysis

The new method does not require any artificial procedure such as chemical separation so that the analysis can be made in full computer basis. When the gamma-gamma coincidence events come to the data acquisition computer, the energy information is gain matched and stored on a two-dimensional matrix in event by event basis. At the same time, the nuclear data like half lives for each nuclide are referenced to determine the quantities of nuclides from the intensities of peaks in the matrix, whereby the result is displayed on a real-time basis on the computer screen. At present, the procedures up to automatic matrix generation have been completed and development of the quantification program is under way.

7. Applications

Neutron activation with coincident gamma-ray detection has been successfully applied to several samples. At first, reference igneous rock and Allende meteorite samples are analyzed and simultaneously thirty elements were identified. The long-lived radioactive nuclide, ^{129}I, is produced in nature or artificially. Neutron activation with coincident gamma-ray detection has turned out to give a reliable and practical tool for its quantification: the detection limit amounts to 10^{-13} for the ^{129}I/^{127}I ratio.[5] Iridium content of geological samples in the Paleozoic and Mesozoic will give us information on the change of earth environment due to meteorite collisions. **Figure 1** shows the detection limit of iridium is 10^{-11}.

III. Summary and Future Perspectives

By combining the gamma-gamma coincidence with neutron activation analysis, we could develop a rapid non-destructive trace element analysis technique, which enables simultaneous quantification of 49 elements with high sensitivity (ppt order at maximum) and high precision (3% except statistical uncertainty). Since chemical separation is not required, we are free from the exposure to radiation. As a

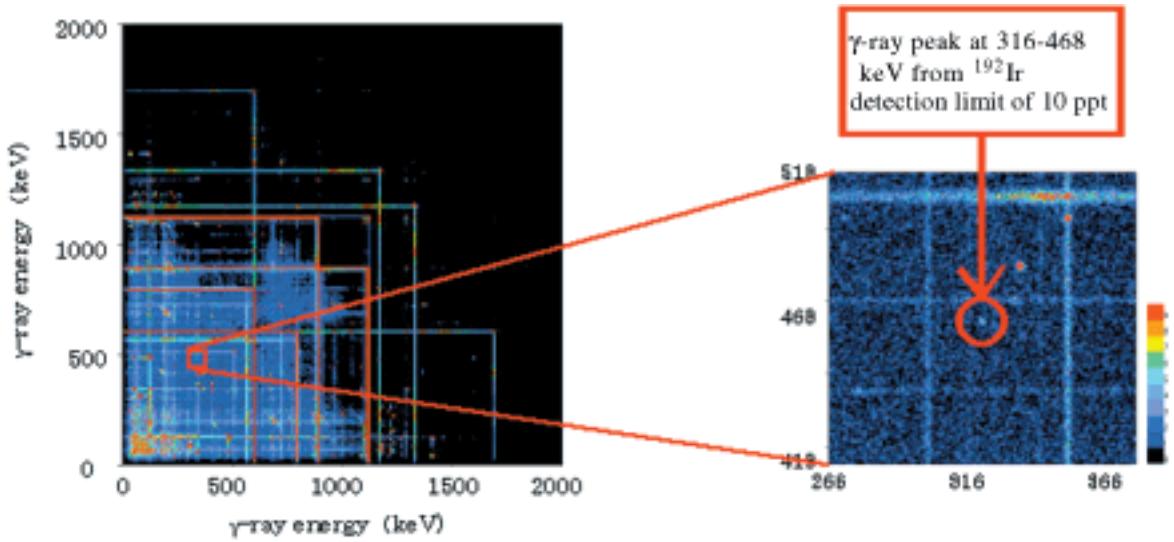

Fig. 1 An example of gamma-gamma matrix obtained for geological sample in the Paleozoic

price for these merits, the other 23 elements are not suited for this method, because the nuclides originating from them do not emit multiple coincident gamma-rays; ordinary one-dimensional method needs to be applied for these elements.

So far we utilized neutrons from research reactors but pulsed neutrons of the Advanced Neutron Sources in JAERI and KEK collaboration will open new possibilities of NAACG. Decay gamma-rays emitted from samples activated with pulsed neutrons will be measured between the pulses so that the transport time from irradiation to measuring position is not needed: short-lived nuclides as well as long-lived ones can be quantified; at the same time high sensitivity due to gamma-ray coincidence measurement is guaranteed. Together with prompt gamma-ray measurement almost all elements are expected to be quantified.

With the recent development of detector technology a large-volume segmented HPGe detector becomes possible. By designing a new detector system utilizing those detectors the detection efficiency and signal-to-noise ratio can be improved. Then we hope to achieve much higher sensitivity than the present.

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