

Determination of trace elements using multi-parameter coincidence spectrometry

Y. Hatsukawa,* Y. Toh, M. Oshima, A. Kimura, M. Hosein Mahmudy Gharai

Japan Atomic Energy Research Institute, Tokai, Ibaraki, 319-1195 Japan

(Received April 13, 2006)

In this study, sensitive trace element analyses were carried out without chemical separation by the combination of neutron activation analysis and multi-parameter coincidence spectroscopy. A long-lived radioisotope ^{129}I in algae samples and iridium in geological samples were analyzed.

Introduction

The method of multi-parameter coincidence spectrometry based on $\gamma\text{-}\gamma$ coincidence is widely used in the field of nuclear structure studies, and has produced many successful achievements. In this study, sensitive trace element analyses were carried out without chemical separation by the combination of neutron activation analysis and multi-parameter coincidence spectroscopy. In the case of neutron activation analysis, measurements of γ -rays from trace elements are strongly interfered by the γ -rays from major elements, e.g., ^{24}Na , ^{56}Mn . Therefore, usually chemical separations are required to eliminate the major elements and to determine the trace elements. Multi-parameter coincidence spectrometry using two detectors already has been applied to neutron activation analysis.^{1–3} This method, however, has the disadvantage of low efficiency.

In the present work, we improved the low efficiency of multi-parameter coincidence spectrometry, with an array of 19 Ge detectors called GEMINI-II.^{4,5} All detectors are equipped with BGO Compton suppressors. Measurements of iridium in geological samples and ^{129}I in algae were carried out with this method.

Experimental

^{129}I

The ratio of $^{129}\text{I}/^{127}\text{I}$ in the algae samples collected from Ibaraki and Hokkaido in Japan was measured by neutron activation analysis. The γ -rays from ^{130}I produced by the $^{129}\text{I}(n,\gamma)^{130}\text{I}$ reaction, were detected using multi-parameter coincidence measurement. About 100 grams of algae was carbonized, and after chemical purification, the iodine was precipitated as PbI_2 . The PbI_2 sample was sealed in a quartz vial and two standard samples containing known amounts of natural iodine and ^{129}I were also prepared. The samples were irradiated for 2–3 hours with neutrons at the JRR-4 research reactor of Japan Atomic Energy Research

Institute. The thermal neutron flux at the irradiation position was $3.3 \cdot 10^{13} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$. After the irradiation, the $\gamma\text{-}\gamma$ coincidence measurements of the PbI_2 and standard samples were carried out using GEMINI-II without any chemical purification. The PbI_2 samples collected from algae were measured for about 24 hours, while the standard samples of ^{129}I and natural iodine measured for 10 hours and 3 hours, respectively. All the samples were measured together with a ^{133}Ba standard source to perform dead-time correction for the detector system. A coincidence matrix of the γ -rays was derived from the detected counts. A peak can be found in the matrix whenever two γ -rays are in coincidence.

Iridium

Iridium can also be determined in geological samples by the multi-parameter coincidence method without chemical separation. In order to evaluate the feasibility of multi-parameter coincidence spectrometry for ultra-trace iridium measurement, 10 standard rock samples were analyzed and the obtained results were compared with the reference values. Iridium concentrations in pelagic deep-sea sediment were also determined using the multi-parameter coincidence γ -ray spectroscopy. The deep-sea sediment samples were provided from Japan Marine Science and Technology Center (JAMSTEC). Deep-sea piston core of 128 cm length was collected from the depth of 5880 m, sampling location was the eastern Philippine sea ($17^\circ 03.5\text{N}$, $130^\circ 15.0\text{E}$). Sedimentation rate was estimated to 3.65 mm/1000 years by paleomagnetic method.⁶ Four samples were taken from the piston core at the position of 15, 41, 58, and 94 cm, which were irradiated and analyzed.

Thirty one hundred mg each of ground homogenized rock or sediment samples were sealed in pure quartz vials, and then irradiated for 15 to 48 hours at the JRR-3 reactor with a neutron flux of $9.6 \cdot 10^{13} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$. 100–200 ng of iridium standard samples were also prepared and irradiated together with the rock samples.

* E-mail: hatsu@popsvr.tokai.jaeri.go.jp

The $\gamma\text{-}\gamma$ coincidence peak of 468–316 keV from ^{192}Ir ($T_{1/2}=73.8$ d) produced by the $^{191}\text{Ir}(n,\gamma)^{192}\text{Ir}$ reaction was used as analytical line. The dead time correction was carried out similarly to the ^{129}I analysis. The iridium concentration of the sediment samples were obtained from the comparison of ^{192}Ir intensities of the sediment samples with the iridium standard.

Results and discussion

A coincidence $E_\gamma\text{-}E_\gamma$ matrix obtained from the PbI_2 extracted from algae sample in Hokkaido is shown in Fig. 1. The figure shows a partial decay scheme of ^{130}I , which includes some dominant gamma-ray energies. In this study, the 536–740 keV pair was analyzed because of low background.

The $\gamma\text{-}\gamma$ coincidence peak can be observed in the matrix at 536–740 keV. The isotopic ratios $^{129}\text{I}/^{127}\text{I}$ is determined to be $5\cdot 10^{-11}$. The ratios measured in this work are listed in Table 1, together with the literature data, and found to be statistically consistent with the previous data set. From the consideration of the obtained peak area, irradiation conditions, detection time, the

detection limit of this method is estimated to be about 10^{-13} of $^{129}\text{I}/^{127}\text{I}$.

The results of iridium measurements of the standard rock samples are shown in Table 2, and the reference values are also listed. All results were in good agreement with previous data. From these data, about 10 ppt of iridium can be determined by this method in geological samples without chemical separations.

A part of two dimensional matrix obtained from deep sea sediment is shown (Fig. 2). A coincidence peak of 468–316 keV was observed in this matrix According to the peak intensity, iridium concentrations of the samples were calculated. The iridium concentrations of the deep-sea sediment samples obtained in this study are 130–248 ppt. These values are relatively high compared to the averaged value of the earth crust samples. It is thought that this high iridium concentration results from a huge contribution of cosmic dust which is rich in iridium. According to the results of this work, we found that the concentration of the iridium in deep-sea sediment is distributed uniformly in the boring core sample.

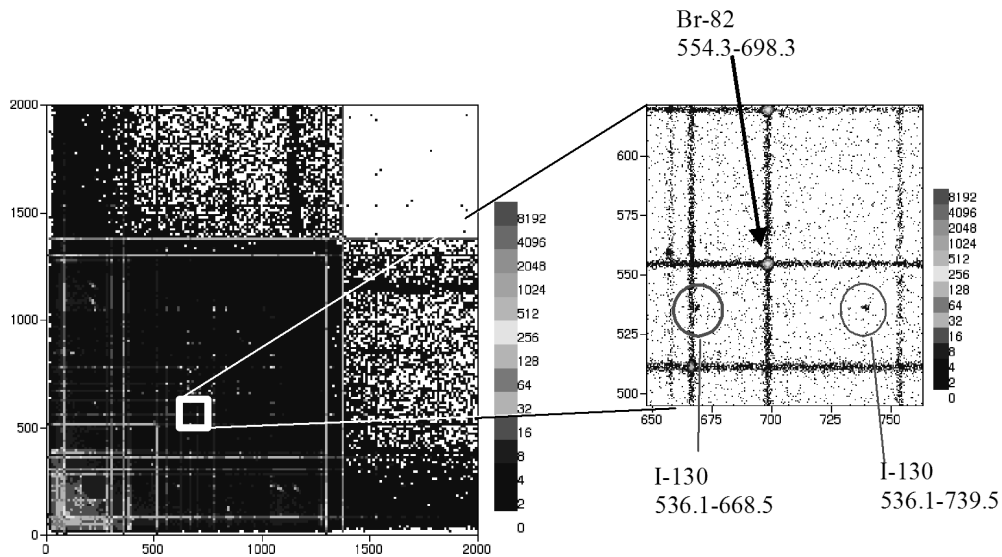


Fig. 1. A two dimensional matrix obtained from PbI_2 sample. Gamma-gamma coincidence peaks of 536–668 keV and 536–739 keV from ^{130}I which produced by the $^{129}\text{I}(n,\gamma)^{130}\text{I}$ reaction can be observed

Table 1. The isotopic ratio $^{129}\text{I}/^{127}\text{I}$ determined in algae samples with the $\gamma\text{-}\gamma$ coincidence method

Sample; scientific name (location)	$^{129}\text{I}/^{127}\text{I}$ ratio
Kajime; <i>Ecklonia</i> (Ibaraki)	$3.5\cdot 10^{-10}$ * This work
Konbu; <i>Laminaria japonica</i> (Hokkaido)	$5\cdot 10^{-11}$ * This work
Funori; <i>Gloiopeltis complanata</i> (Ibaraki)	$5.1\cdot 10^{-9}$ **
Higiki; <i>Hizikia fusiforme</i> (Ibaraki)	$3.3\cdot 10^{-9}$ **
Wakame; <i>Undaria pinnatifida</i> (Ibaraki)	$<1\cdot 10^{-9}$ **

* Ref. 7.

** Ref. 8.

Table 2. Iridium measurements in standard rock samples and reference values

Sample name	This work, ppb	Reference value,* ppb
PTM-1	430 (15)	300
PTC-1	301 (16)	–
WMS-1	104 (10)	100
SARM-7	87 (14)	74
WPR-1	16.4 (1.4)	–
JP-1	2.2 (0.6)	2
DNC	0.55 (0.04)	0.52
BIR-1	0.20 (0.05)	0.15
W-2	0.08 (0.01)	–

* Ref. 9.

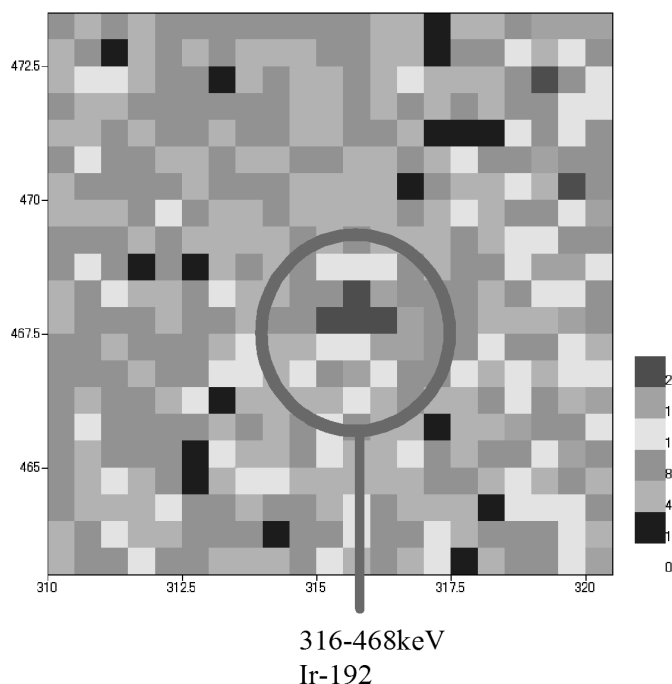


Fig. 2. A part of two dimensional matrix obtained from deep-sediment sample which is collected at 94 cm from the top of the core. Gamma-gamma coincidence peak of 468–316 keV can be observed

Conclusions

In this work, long-lived radio isotope, ^{129}I , in sea weed in Japan was determined to be $3.5 \cdot 10^{-10}$ to $5 \cdot 10^{-11}$ of $^{129}\text{I}/^{127}\text{I}$ using multi-parameter coincidence spectrometry based on γ - γ coincidence. The detection limit of this method was estimated to be $^{129}\text{I}/^{127}\text{I} = 10^{-13}$. Iridium contents in various geological samples were determined. About 10 ppt of iridium in geological sample can be determined by this method without chemical separations.

Reference

1. J. W. MORGAN, W. D. EHMANN, *Anal. Lett.* 2 (1969) 537.
2. G. MEYER, *J. Radioanal. Nucl. Chem.*, 114 (1987) 223.
3. CH. KOEBERL, H. HUBER, *J. Radioanal. Nucl. Chem.*, 244 (2000) 655.
4. K. FURUNO, M. OSHIMA, T. KOMATSUBARA, K. FURUTAKA, T. HAYAKAWA, M. KIDERA, Y. HATSUKAWA, M. MATSUDA, S. MITARAI, T. SHIZUMA, T. SAITOH, N. HASHIMOTO, H. KUSAKARI, M. SUGAWARA, T. MORIKAWA, *Nucl. Instr. Meth.*, A421 (1999) 211.
5. Y. HATSUKAWA, M. OSHIMA, T. HAYAKAWA, Y. TOH, N. SHINOHARA, *Nucl. Instr. Meth.*, A482 (2002) 328.
6. M. OKADA, private communication.
7. Y. TOH, Y. HATSUKAWA, M. OSHIMA, N. SHINOHARA, T. HAYAKAWA, K. KUSHITA, T. UENO, *Health Phys.*, 83 (2002) 110.
8. Y. MURAMATSU, Y. OHMOMO, D. CHRISTOFFER, *J. Radioanal. Nucl. Chem.*, 83 (1984) 353.
9. P. J. POTTS, A. G. TINDLE, P. C. WEBB, *Geochemical Reference Material Compositions*, CRC Press, Boca Raton, FL, 2000.