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PROMPT GAMMA-RAY ANALYSIS USING COLD AND THERMAL GUIDED NEUTRON BEAMS

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A permanent and stand-alone neutron-induced prompt γ-ray analysis (PGA) system, usable at both cold and thermal neutron beam guides of JRR-3M has been constructed. The characteristics of the system, including neutron beam and γ-ray spectrometer were measured. Owing to the absence of fast neutrons and the low γ-ray background, analytical sensitivities and detection limits better than those in other PGA systems have been achieved. Analytical results of ten elements in Standard Reference Material of Coal Fly Ash agreed well with those obtained by other methods. Isotopic analysis of Ni and its application to accurate and precise determination of Ni by stable isotope dilution method were performed.

Neutron-induced prompt γ-ray analysis (PGA)[1] is characterized by its capability for nondestructive multi-elemental analysis and by its ability for analyzing H, B, N, S, P, Si and Cd which are difficult to analyze by instrumental neutron activation analysis (INAA). Because of poor beam quality, previous thermal neutron PGA facilities[2,3] provide lower analytical sensitivity and higher detection limits than those for facilities using guided neutron beams. PGA has thus been regarded only as complementary to INAA. Cold and thermal neutron beams guided by a Ni coated glass mirror tube are virtually free of γ-rays, fast and epithermal neutrons. Earlier studies[4-6] indicated that PGA using a guided neutron beam has improved analytical sensitivity and detection limit. The absence of γ-rays, fast and epithermal neutrons permits the detector to be placed closer to the sample. In addition, the neutrons in the guide beam are shifted to a lower energy, resulting in an increased effective capture cross sections.

A permanent and stand-alone PGA system, usable at both cold and thermal neutron beam guides of JRR-3M has been constructed[7,8], similar to those of the National Institute of Standards and Technology (NIST)[9] and the Research Center (KFA) Jülich[10]. The design concept is to achieve the lowest γ-ray background. To achieve this, 1) neutron shielding materials, lithium fluoride (LiF) tiles and fluorocarbon resin, are used as construction materials at positions near the sample, 2) the sample box is filled with He gas, and 3) Ge-BGO detectors

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are used to lower the Compton background. In this paper, the characteristics of the system and applications of the PGA system for elemental and isotopic analysis are described.

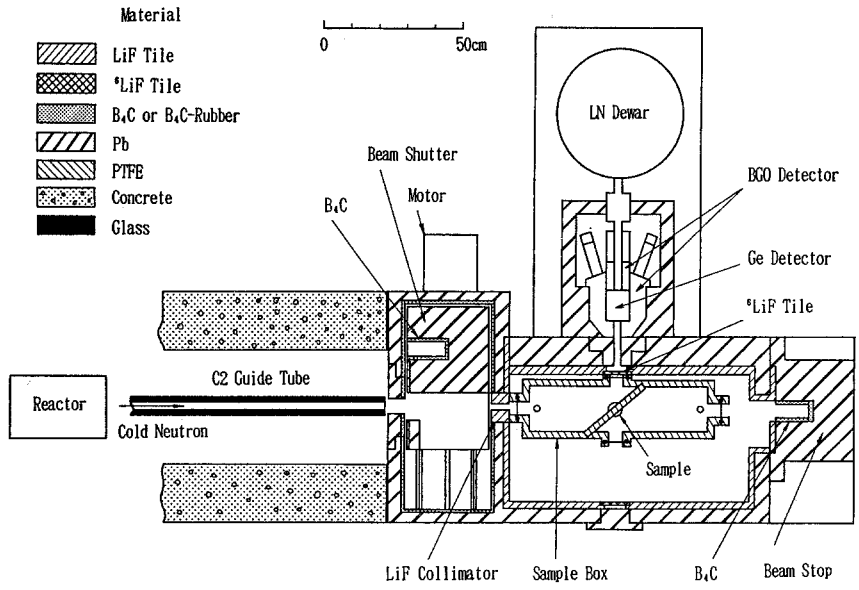

Figure 1 Layout of JRR-3M PGA system at the cold neutron beam guide

Experimental

Apparatus: The PGA system can be placed either at the cold (C2-3-2) or the thermal (T1-4-1) neutron beam guide of JRR-3M (20 MW). Initially, the present system was placed behind a 4 m extended guided tube at the cold neutron beam port (C2-3-2)[7,8]. For higher neutron flux and better homogeneity, the system has been improved by placing the apparatus directly at the cold neutron guide without the extended guided tube. The layout of the system at the cold neutron beam guide is shown in Figure 1. The neutron flux at the sample position were 1.4×10^8 and 2.4×10^7 n cm^{-2} s^{-1} for the cold and thermal neutron beams, respectively. The peak neutron energy (wave length) of the cold and thermal neutron distributions were 3.0 meV (520 nm) and 15 meV (230 nm), respectively. The system consists of a neutron beam shutter, a neutron beam collimator, a sample box, a neutron beam stopper, shielding for neutrons and γ-rays, and a multi-mode γ-ray spectrometer. To achieve the lowest γ-ray background, neutron shielding materials, lithium fluoride tiles (LiF, ^{6}LiF), and polytetrafluoroethylene (PTFE) are used as construction materials at the position near the samples, and the sample box made with PTFE is filled with He gas. The neutron beam is collimated to 20×20 mm^2 by LiF collimator.

The multi-mode γ-ray spectrometer consists of a closed end coaxial type high purity Ge detector, BGO (bismuth germanate, $Bi_4Ge_3O_{12}$) shielding detectors, and a pulse height analyzer (PHA) system controlled by a personal computer. Three modes of prompt γ-ray measurements: a single mode, a Compton suppression mode, and a pair mode, in the energy range of 0 to 12 MeV, can be performed simultaneously. The neutron beams were monitored continuously by measuring scattered neutrons with a ^{3}He counter set beside the sample box and also by measuring prompt γ-rays from 0.05 and 0.5 mm thick Ti plates for the cold and thermal neutrons, respectively. A detailed description of the PGA system can be found elsewhere[7].

Analytical procedure: A known amount of sample was wrapped in 25 μm thick fluorinated ethylenepropylene resin (FEP) film of an area smaller than 15 × 15 mm^2 and was heat sealed. The wrapped sample was mounted on a PTFE sample holder using PTFE string of 0.3 mm (diameter) and was then placed in an air-tight PTFE sample box. The air in the box was purged using He gas flow. The three modes of γ-ray spectra in the energy range of 0 to 12 MeV were acquired for 500 to 50000 s while passing He into the box at a flow rate of about 1000 ml/min.

Results and Discussion

Characteristics of the system: The neutron flux at the sample position was measured by irradiating a Au foil as previously described[7]. The average neutron flux of the cold and thermal neutron beams in the 20 × 20 mm^2 area were 1.4 × 10^8 and 2.4 × 10^7 n cm^{-2} s^{-1} with the relative standard deviation 18 and 5 % for the cold and thermal neutrons, respectively. Formerly when an extended guide tube was used the neutron flux was 1.1 × 10^8 n cm^{-2} s^{-1} with a coefficient of variation of 34 % for cold neutron beam[7]. The neutron flux and homogeneity of the neutron beam were improved by positioning the system directly at the cold neutron beam port. The flux fluctuation measured by prompt γ-rays of Ti plates at the sample position of the neutron beam during one reactor operation cycle (26 days) was 0.8 and 1.0 % for the cold and thermal neutrons, respectively.

The neutron flux was increased by 8.5 % and γ-ray background was reduced drastically by purging air in the sample box with He gas. In the previous PGA systems such as University of Maryland-NIST[3] and University of Missouri[2] which use direct neutron beams from reactor core, the background prompt γ-rays of H and other elements of the construction materials are up to 166 times greater than the background of the present system. This is mainly due to the presence of γ-rays, fast and epithermal neutrons in the beams of the other systems. In those systems, a large amount of moderating and shielding materials are required to eliminate undesired neutrons. In the present system, however, such large amounts of shielding are not necessary. However decay γ-rays of natural ^{207}Bi in the BGO detectors were detected in the background spectrum of the present system.

To demonstrate the multi-elemental analytical ability of the system and to compare with other existing systems, the analytical sensitivities and detection limits of 73 elements were measured at

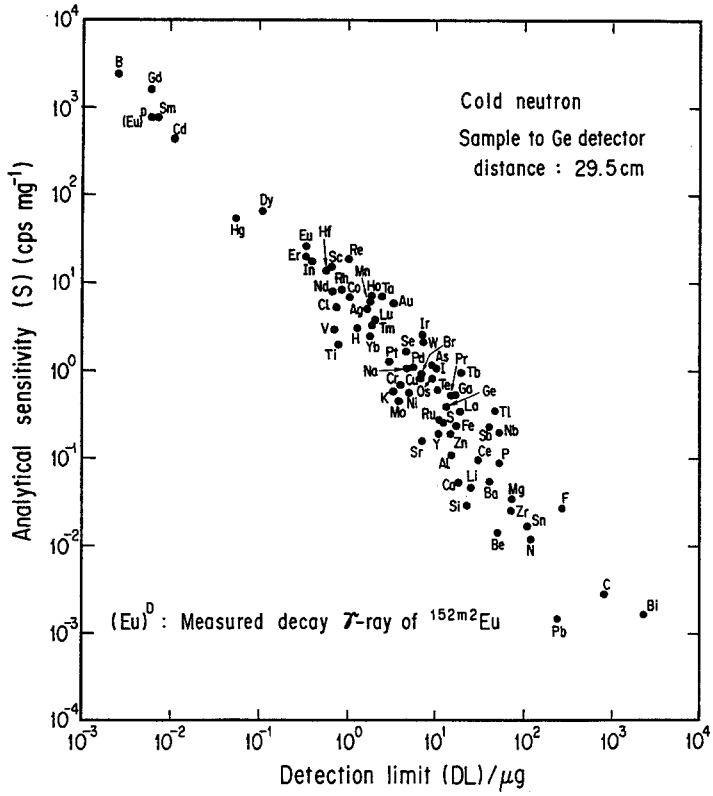

Figure 2 Plot of analytical sensitivity (S) versus detection limit (DL) of the elements measured at the cold neutron beam after improvement

both cold and thermal neutron beams. The analytical sensitivities were obtained from the measurements of prompt γ-ray spectra of standard samples. From the Compton suppression spectrum of a known amount of FEP film, the 3σ background count in the region corresponding to the prompt γ-ray line of a specified element was estimated to calculate the detection limit. A plot of the highest analytical sensitivity versus the lowest detection limits of the elements at the cold neutron beam after improvement is shown in Figure 2. Boron, Sm, Gd, and Cd are the elements having the highest analytical sensitivity with detection limits down to 1-10 ng. Mercury, Dy, Eu, Er, Nd, In, Hf, Cl, Sc, Ti, Co, and H can be detected to 0.05-1 μg. Lead, F, C, and Bi have the lowest sensitivity with detection limits in the range of 0.2-2 mg. Other elements are considered to have a medium sensitivity, such as V, Yb (and most of the other lanthanides), Mn, Ag, Ni, Na, K, S, Fe, Si, P, Sn, and N, etc. with detection limits ranging from 1-100 μg. Before the improvement, i.e. when the extended guided tube was used at the cold neutron beam[7,8], the analytical sensitivities of these elements were 1.4 to 2 times lower.

The analytical sensitivities of these elements are 5.3 to 12 times lower for the thermal neutron irradiation. The sensitivity of the present system at the cold neutron beam is up to about 5 times higher than the values reported for the University of Maryland-NIST[3] and the University of Missouri[2] systems. The detection limits of the present system at the cold neutron beam are lower that those of a similar system at the NIST Cold Neutron Research Facility[13].

Elemental analysis: Applications to multi-elemental analysis in several materials were studied. The prompt γ-ray Compton suppression spectrum of the Coal Fly Ash measured at the cold neutron beam is shown in Figure 3. The prompt γ-ray peaks of H, B, Al, Si, K, Ca, Ti, Fe, Sm and Gd are detected. The S/N ratio of the present data as compared to that from the University of Maryland-NIST[11] system for the same sample was found to be higher by a factor of 4 to 8 for Gd, Fe and B, but for Sm it was only 1.3. A beam type PGA system like that of the University of Maryland-NIST contains γ-rays, fast and epithermal neutrons in the beam, thus the γ-ray background is high, especially in the low energy region. However, the guide beam type system is almost free of γ-rays, fast and epithermal neutrons, so that the S/N ratios for Gd, Fe, and B are much higher. For the case of Sm, its higher resonance capture cross section for epithermal neutrons results in an S/N ratio no better than that of the University of Maryland-NIST system. From the peak area of most sensitive and interference free γ-ray line of the element in the samples and standards, multi-elemental concentrations were calculated. The analytical results are shown in Table 1 together with those obtained by other methods. Good agreement was achieved between the results of present method and those obtained by other methods.

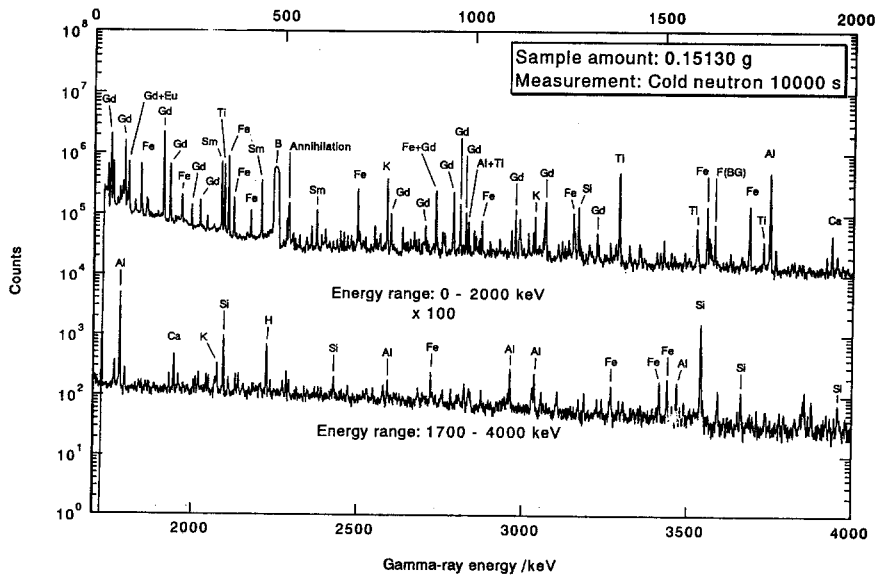

Figure 3 Prompt γ-ray Compton suppression spectrum of Coal Fly Ash NIST 1633a

Due to large cross section of the reaction $^{10}B(n,\alpha)^{7*}Li$ (σ = 3837 barn), the Doppler broadened 478 keV photo-peak is observed with the highest sensitivity by PGA. The present PGA is being applied to the determination of ppb to ppm levels of B in materials, biological, geological and environmental samples. It is also used for the rapid determination of ^{10}B in blood, urine and tumor during the brain-tumor treatment by boron neutron capture therapy (BNCT). Multi-elemental analysis was applied to several reference materials such as rocks, biological samples, sediments (pond, marine, river), coal, oil, human hair and several environmental samples, and satisfactory results were obtained.

Isotopic analysis: The PGA is useful not only for elemental analysis, but for isotopic analysis. The isotopic analysis of Ni and Si which is difficult by mass spectrometer has been examined. Natural Ni consists of 5 stable isotopes of ^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni and ^{64}Ni. The Compton suppression prompt γ-ray spectra of natural isotopic composition of Ni and ^{60}Ni

Table 1

Analytical results of Coal Fly Ash NIST 1633a

Element	Unit	E_γ keV	Content, % or ppm					
			Present method			Av.	Other method a	b
H	%	2224	0.039,	0.053,	0.057	0.050		
B	ppm	478	37.8,	39.3,	39.2	38.8	39.2 ± 0.7	
Al	%	1779	16.5,	15.2,	15.3	15.7	14.0 ± 0.2	14.3 ± 1.0
Si	%	3540	25.7,	21.9,	21.7	23.1	22.2 ± 0.4	22.8 ± 0.8
K	%	770	2.24,	1.99,	2.03	2.09	1.97 ± 0.04	1.88 ± 0.06
Ca	%	1942	1.36,	1.16,	1.14	1.22	1.29 ± 0.11	1.11 ± 0.01
Ti	%	342, 1381	0.954,	0.925,	0.871	0.917	0.840 ± 0.01	(0.8)
Fe	%	352	10.2,	9.69,	9.07	9.66	9.7 ± 0.2	9.4 ± 0.1
Sm	ppm	334	17.4,	17.3,	15.7	16.8	16.0 ± 0.2	
Gd	ppm	182	16.2,	16.2,	14.6	15.6	15.3 ± 0.2	

a: Neutron capture prompt γ-ray activation analysis (Ref.11);

b: NIST certified value, value in parenthesis is information value, not certified.

enriched (99.65 % enrichment) isotope are shown in Figure 4. The prompt γ-ray lines of Ni could be assigned by measuring enriched isotopes of ^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni and ^{64}Ni. The isotopic analysis of Ni is applied to accurate and precise determination of Ni by stable isotope dilution method similarly to a isotope-dilution neutron activation analysis (IDNAA)[14]. In the case of the isotope-dilution PGA (IDPGA), the Ni amounts W_{nat} (g) in the sample can be

calculated by the following equation:

$$W_{nat} = W_{sp} \frac{M_{nat}}{M_{sp}} \cdot \frac{\frac{K_{sp,i}}{K_{nat,i}} R_{mix} - \frac{K_{sp,j}}{K_{nat,j}} R_{nat}}{R_{nat} - R_{mix}}$$

where W_{sp} (g) is the amount of enriched spike element, M_{nat} and M_{sp} are the atomic weights of natural and spike elements, $K_{sp,i}$, $K_{nat,i}$, $K_{sp,j}$ and $K_{nat,j}$ are isotopic compositions of i and j isotope in natural and spike, R_{nat} and R_{mix} are the count rate ratios of isotope i to j for the natural and spiked mixture. The IDPGA was applied to the determination of Ni in reference materials of Stainless steel (JSS 652-7) using enriched ^{60}Ni as spike, and measuring the prompt

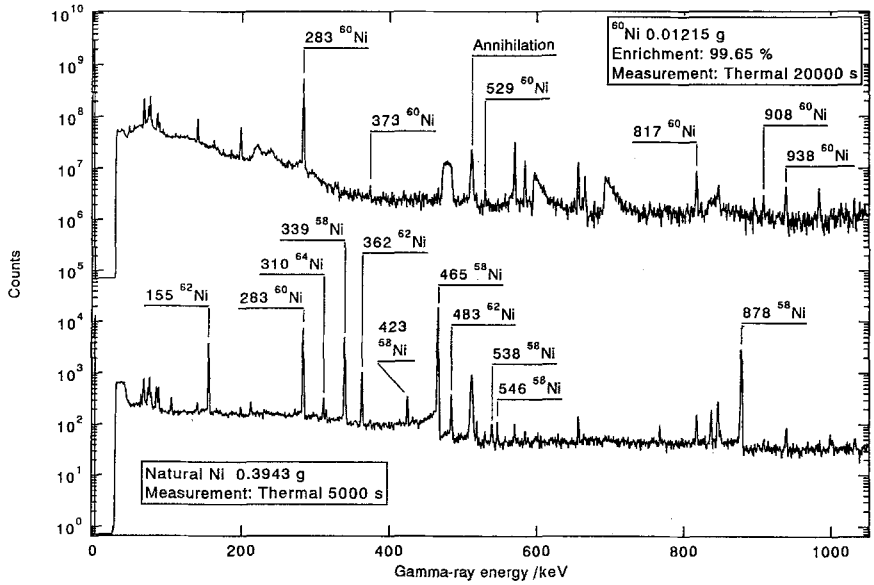

Figure 4 Prompt γ-ray Compton suppression spectra of ^{60}Ni and natural Ni

γ-rays from ^{58}Ni and ^{60}Ni. The analytical results of five independent analysis 11.51 ± 0.18 % agreed well with the standard value of the sample 11.31 ± 0.028 % with relative standard deviation of 1.6 %. Isotopic analysis of ^{28}Si, ^{29}Si and ^{30}Si were also examined by the PGA.

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