Improved method for measuring low concentration radium and its application to the Super-Kamiokande Gadolinium project

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Chemical extraction using a molecular recognition resin named “Empore Radium Rad Disk” was developed to improve sensitivity for the low concentration of radium (Ra). Compared with the previous method, the extraction process speed was improved by a factor of three and the recovery rate for $^{226}$Ra was also improved from $81\pm4\%$ to $>99.9\%$. The sensitivity on the $10^{-1}$ mBq level was achieved using a high purity germanium detector. This improved method was applied to determine $^{226}$Ra in Gd$_2$(SO$_4$)$_3$·8H$_2$O which will be used in the Super-Kamiokande Gadolinium project. The improvement and measurement results are reported in this paper.

1. Introduction

Detection of radium (Ra) is important not only for environmental studies, medical science, biology, but also for non-accelerator particle physics experiments (e.g. neutrino measurements and dark matter searches), which require a low background experimental environment. In general, short lifetime radioactive materials (e.g. $^{226}$Ra) are measured using particle counters such as $\alpha$-spectrometers, liquid scintillators, and germanium detectors. However, the sensitivity is generally limited by the detection efficiency related to the sample size, i.e. self-shielding effect and geometrical acceptance. To minimize these problems and improve sensitivity, chemical extraction is often used. For example, Dulanská et al., [1] have used a molecular recognition resin named “AnaLig-Sr01”, which is a product of IBC Advanced Technologies [2]. They determined the concentration of $^{226}$Ra included in rocks or building materials in the range of $5.2 - 165.0$ Bq kg$^{-1}$. Other chemical extraction techniques have
been developed using “Empore Radium Rad Disk” produced by 3M Corporation [3] (see the following sections in more details) to determine $^{226}\text{Ra}$ in water at the $10^{-2}$ – $10^{-4}$ mBq L$^{-1}$ level [4–6]. However, the chemical extraction of $^{226}\text{Ra}$ from a very high matrix sample with a much lower concentration has not been established.

The Super-Kamiokande Gadolinium (SK-Gd) project is an upgrade of the Super-Kamiokande (SK) detector [7], with its final goal of dissolving gadolinium sulfate octahydrate ($\text{Gd}_2(\text{SO}_4)_3\cdot8\text{H}_2\text{O}$) into the SK detector up to the 0.2% concentration [8, 9]. One of the main physics targets of SK-Gd is to discover supernova relic neutrinos and study star formation of the universe [10]. The measurements of solar neutrinos with a low energy threshold of $\sim3.5$ MeV [11] will be also continued in SK-Gd: therefore several radio impurities (e.g. $^{226}\text{Ra}$, $^{238}\text{U}$, and $^{232}\text{Th}$) in $\text{Gd}_2(\text{SO}_4)_3\cdot8\text{H}_2\text{O}$ should be minimized before loading into SK. The maximum allowed level of these radio impurities in $\text{Gd}_2(\text{SO}_4)_3\cdot8\text{H}_2\text{O}$ [12, 13] and the typical example of a commercially available product are summarized in Table 1. For the measurement of $^{238}\text{U}$ and $^{232}\text{Th}$, the procedure was developed using inductively coupled plasma-mass spectrometry (ICP-MS) with chemical extraction (see Ref. [14] for more details).

As shown in Table 1, SK-Gd requires a method to determine low concentration $^{226}\text{Ra}$. However, the sensitivity for $^{226}\text{Ra}$ of the previous method with the molecular recognition resin “AnaLig-Ra01” was on the 1 mBq level [16]. In addition, the recovery rate of $^{226}\text{Ra}$ with the previous method was 81±4% and the process time of the sample was 1 L per hour. To achieve the required sensitivity of SK-Gd, it was necessary to increase the concentration rate with a higher recovery rate and a shorter processing time. In this study, the procedure of chemical extraction was improved to achieve the sensitivity of on the $10^{-1}$ mBq kg$^{-1}$ level by solving these problems: the improved method was applied to SK-Gd to determine the concentration of $^{226}\text{Ra}$ in $\text{Gd}_2(\text{SO}_4)_3\cdot8\text{H}_2\text{O}$.

Table 1 Summary of the maximum allowed level for SK-Gd and the typical values of commercially available product [12, 13]. All units are mBq kg$^{-1}$ ($\text{Gd}_2(\text{SO}_4)_3\cdot8\text{H}_2\text{O}$).

| Requirement for SK-Gd | $^{226}\text{Ra}$ | $^{238}\text{U}$ | $^{232}\text{Th}$ |
|-----------------------|------------------|------------------|------------------|
| The typical concentration of commercially available product | 0.5 | 5 | 0.05 |
| | 5 | 50 | 100 |

2. Experimental equipment

2.1. Chemical equipment

“Empore Radium Rad Disk” [3] was used for chemical extraction. The resin with the same chemical features as AnaLig-Ra01 was positioned on a filter (47 mm diameter and 0.5 μm thickness) made of polytetrafluoroethylene fibrils. Figure 1 shows the experimental setup of the chemical extraction using a vacuum filtration system with the disk. The disk was placed on a holder with the volume of 800 mL (Advantech Toyo Ltd. [17], KP-47), and the holder was connected to the vacuum container (Advantech Toyo Ltd. [17], VT-500). The solution

1 This is generally called “disk” and simply called disk in this paper from now on.
passes through the disk, and $^{226}$Ra in the solution is adsorbed by the resin bedded to the
disk. The concentration of $^{226}$Ra can be determined by measuring the disk directly using an
HPGe detector.

To produce solutions with low contamination, ultra-pure SK water [7] was used. Electronic
grade 70% nitric acid (HNO$_3$) (Wako Pure Chemical Industries Ltd. [18]) was used to wash
the disk and efficiently dissolve Gd$_2$(SO$_4$)$_3$·$8$H$_2$O in the SK water.

To easily check the concentration of $^{226}$Ra in Gd$_2$(SO$_4$)$_3$·$8$H$_2$O, $^{226}$Ra-rich hot spring
water from the Kawakita hot spring in Ishikawa, Japan [19] was used as the calibration
solution. The concentration of $^{226}$Ra in the hot spring water was $112^{+34}_{-12}$ mBq L$^{-1}$, which
was determined by the HPGe detector measurement. The uncertainty was mainly due to
the systematic uncertainty of the HPGe detector (+30% or -10%) and statistics [16]. The
sampled hot spring water was filtrated by membrane filters with the pore size of 0.45 µm
and acidified to pH≈1 by HNO$_3$ for preservation.

Because barium (Ba) and Ra have similar chemical features and ionic radii, Ba is frequently
used as a tracer for Ra analysis to estimate the recovery rate [20]. Thus, 1000 mg L$^{-1}$ Ba
of standard solution (Merck Ltd. [21]) was used to estimate the recovery rate. The details
of studies for the recovery rate are described in Sec. 3. The ICP-MS “Agilent 7900” [22]
was used to measure the concentration of Ba to estimate the recovery rate of $^{226}$Ra. The
performance of this ICP-MS is described in Ref. [14].

Fig. 1  (A) Photograph of the entire experimental setup. (B) Top view of the setup. (C)
Top view of the disk (47 mm diameter).
2.2. High purity germanium detector and its detection efficiency

The HPGe detector used for this measurement was a coaxial p-type HPGe crystal manufactured by CANBERRA France [23]. The dimension of sample chamber was $23 \times 23 \times 48$ cm$^3$. The details of the performance of the HPGe detector are described in Ref. [16]. The samples measured by the HPGe detector were covered by an ethylene vinyl alcohol bag to keep radon from samples inside the bag (Fig. 2).

The concentration of $^{226}$Ra was evaluated using the characteristic $\gamma$-lines of $^{214}$Pb (609 keV) and $^{214}$Bi (352 keV and 1764 keV), which are daughter nuclei of $^{226}$Ra, by considering of their branching ratios and detection efficiencies. Figure 3 shows the typical observed energy spectra for $^{214}$Bi 352 keV measurements. The detection efficiency was evaluated by the Monte Carlo simulation [24]. For example, the detection efficiency of 352 keV gamma rays originating from $^{214}$Bi, with the chemical extraction procedure using the disk was found to be 15.9%. On the other hand, the detection efficiency of 352 keV gamma ray for $^{226}$Ra was determined to be 0.8% for the direct measurement of 5 kg of Gd$_2$(SO$_4$)$_3$·8H$_2$O without a chemical extraction procedure. The detection efficiency was improved by a factor of 20 owing to the smaller volume of the sample using the disk.

![Fig. 2 Setup for the disk measurement with the HPGe detector.](image)

3. Chemical extraction of $^{226}$Ra from Gd$_2$(SO$_4$)$_3$·8H$_2$O and its performance

The setup shown in Fig. 1 was connected to a vacuum pump: the solution loaded into the holder could pass through the disk. The disk was initially washed by loading 50 mL of 3 mol L$^{-1}$ HNO$_3$ and 50 mL of the ultra-pure SK water into the holder. A total of 500 g Gd$_2$(SO$_4$)$_3$·8H$_2$O was dissolved in 10 L of a 0.2 mol L$^{-1}$ HNO$_3$ solution. Then, the sample solution was loaded into the holder, and the vacuum pressure was adjusted to produce a flow rate of 50 mL min$^{-1}$ (3 L per hour, which is a three times faster processing time than that
used in the previous method [16]). Then, the disk was directly placed on the HPGe detector and measured.

The blank amount of $^{226}\text{Ra}$ in the disk was evaluated by measuring 17 disks using the HPGe detector, the value of $1.9^{+0.6}_{-0.3}$ mBq was obtained for 17 disks (corresponding to $0.11^{+0.04}_{-0.02}$ mBq for each disk). In the previous method [16], the value of procedure blank was $0.3\pm0.2$ mBq. This improved the detection limit.

The recovery rate of this procedure was evaluated using the $^{226}\text{Ra}$-rich hot spring water. The volume of 3 mL and 100 mL of the hot spring water was added to 10 L of a Gd$_2$(SO$_4$)$_3$·8H$_2$O dissolved sample solution. Then, the concentration of $^{226}\text{Ra}$ adsorbed by the disk was measured using the HPGe detector for 4.5 days. As shown in Table 2, the results of measurements were consistent with the expected amount of $^{226}\text{Ra}$, and the achieved sensitivity was on the $10^{-1}$ mBq level owing to the development of this chemical extraction procedure.

To estimate the recovery rate more accurately, Ba standard solution was added to the sample solution. The sample solution with the concentration of $4.0\times10^{-8}$ g (Ba) mL$^{-1}$ was loaded into the holder, and the solution (which passed through the disk) was collected and measured using the ICP-MS. The concentration of remaining Ba in the solution was $<0.1\%$. Those studies indicated that high matrix elements (Gd$_2$(SO$_4$)$_3$·8H$_2$O) did not interfere with the extraction of $^{226}\text{Ra}$ and the recovery rate obtained using the developed method was estimated to be $>99.9\%$. This is a significant improvement from the recovery rate obtained using the previous method (81±4%) [16].”

Table 3 shows the comparison of performance between the previous method in Ref. [16] and the developed method in this study. This result shows the sensitivity of the improved
method is on the $10^{-1}$ mBq level and sufficient for measuring the experimentally allowed level of $^{226}$Ra for SK-Gd.

Table 2  Summary of the study for the recovery rate. The blank of the disk was already subtracted.

| Hot spring water (mL) | Expected amount of $^{226}$Ra (mBq) | Results (mBq) |
|----------------------|-------------------------------------|---------------|
| 3                    | $0.33^{+0.10}_{-0.04}$              | $0.40^{\pm0.2}$ |
| 100                  | $11.2^{+3.4}_{-1.2}$                | $11.3^{+3.4}_{-1.3}$ |

Table 3  Summary of the performance in the previous and developed methods.

|                         | Previous method | Developed method |
|-------------------------|-----------------|------------------|
| Recovery rate (%)       | 81±4            | >99.9            |
| Process time for sample (L per hour) | 1               | 3               |
| Procedure blank (mBq)   | 0.3±0.2         | 0.11^{+0.04}_{-0.02} |
| Sensitivity of the test sample (mBq) | 0.9±0.5 | 0.4±0.2 |

4. Application to SK-Gd and results of measuring $\text{Gd}_2(\text{SO}_4)_3\cdot8\text{H}_2\text{O}$

SK-Gd will be conducted in several experimental phases. For the first experimental phase, 13 tons of $\text{Gd}_2(\text{SO}_4)_3\cdot8\text{H}_2\text{O}$ will be dissolved in the SK tank corresponding to a 50% neutron tagging efficiency [9]. $\text{Gd}_2(\text{SO}_4)_3\cdot8\text{H}_2\text{O}$ was produced with many lots: thus, all the lots should be measured before loading. Currently, 14 tons of $\text{Gd}_2(\text{SO}_4)_3\cdot8\text{H}_2\text{O}$ are being measured using the developed method to confirm that their radio impurities are below the experimentally allowed levels (see Table 1). The concentration of $^{226}$Ra in $\text{Gd}_2(\text{SO}_4)_3\cdot8\text{H}_2\text{O}$ (unit: mBq kg$^{-1}$) can be obtained from the amount of $^{226}$Ra measured in the disk divided by the weight of $\text{Gd}_2(\text{SO}_4)_3\cdot8\text{H}_2\text{O}$. Table 4 shows the results of the measurement of $^{226}$Ra in $\text{Gd}_2(\text{SO}_4)_3\cdot8\text{H}_2\text{O}$ for several production lots determined using the improved chemical extraction method. The signals of $^{214}$Pb and $^{214}$Bi were not observed above the statistical uncertainty. The concentrations of $^{226}$Ra in the measured products were confirmed to be below the experimentally allowed level.

On the basis of these studies and measurements, a highly sensitive method for measuring low concentration $^{226}$Ra was established. This method can be applied to other non-accelerator particle physics experiments as well. For example, the XENON-1T detector will be upgraded to the XENON-nT detector with a neutron veto system which is based on a high-purity Gd-loaded water Cherenkov detector [25].

5. Conclusion

The method for measuring $^{226}$Ra using an HPGe detector with chemical extraction was improved to determine low concentration $^{226}$Ra in a high matrix sample. More than 99.9% of $^{226}$Ra was recovered from the high matrix sample with a shorter processing time of the
Table 4  Summary of the measurements of Gd$_2$(SO$_4$)$_3$·8H$_2$O. The upper limits represent 90% confidence level.

| Lot No. | Concentration of $^{226}$Ra (mBq kg$^{-1}$) | Measurement time (day) |
|---------|-------------------------------------|------------------------|
| 1       | < 0.4                               | 6.0                    |
| 2       | < 0.3                               | 11.0                   |
| 3       | < 0.3                               | 8.8                    |
| 4       | < 0.2                               | 9.6                    |
| 5       | < 0.5                               | 8.7                    |
| 6       | < 0.2                               | 13.0                   |

chemical extraction, which resulted in the sensitivity on the 10$^{-1}$ mBq level. The improved method is being applied to SK-Gd to determine $^{226}$Ra in Gd$_2$(SO$_4$)$_3$·8H$_2$O. Currently, all the measured Gd$_2$(SO$_4$)$_3$·8H$_2$O products, which will actually be loaded into the SK tank, were confirmed to be below than the maximum allowed $^{226}$Ra concentration level.

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