

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 ²²⁶Ra was also improved from $81 \pm 4\%$ 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 ²²⁶Ra in $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ which will be used in the Super-Kamiokande Gadolinium project. The improvement and measurement results are reported in this paper.
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1. Introduction

Detection of radium (Ra) is important not only for environmental studies, medical science and 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. ²²⁶Ra) are measured using particle counters such as α -spectrometers, liquid scintillators, and germanium detectors. However, the sensitivity is generally limited by the detection efficiency related to the sample size, i.e. the 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 ²²⁶Ra 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 the “Empore Radium Rad Disk” produced by 3M Corporation [3] (see the following sections for more details) to determine ²²⁶Ra in water at the $10^2 - 10^4$ mBq L⁻¹ level [4–6]. However, the chemical extraction of ²²⁶Ra 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 the final goal of dissolving gadolinium sulfate octahydrate ($\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$) into the SK detector up to the 0.2% concentration [8,9]. One of the main physics targets of SK-Gd is

Table 1. Summary of the maximum allowed level for SK-Gd and the typical values of commercially available products [12,13]. All units are mBq kg⁻¹ (Gd₂(SO₄)₃·8H₂O).

| | ²²⁶ Ra | ²³⁸ U | ²³² Th |
|--|-------------------|------------------|-------------------|
| Requirement for SK-Gd | 0.5 | 5 | 0.05 |
| The typical concentration of commercially available products | 5 | 50 | 100 |

to discover supernova relic neutrinos and study star formation of the universe [10]. The measurements of solar neutrinos with a low energy threshold of ~ 3.5 MeV [11] will also be continued in SK-Gd: therefore several radio impurities (e.g. ²²⁶Ra, ²³⁸U, and ²³²Th) in Gd₂(SO₄)₃·8H₂O should be minimized before loading into SK. The maximum allowed level of these radio impurities in Gd₂(SO₄)₃·8H₂O [12,13] and the typical example of a commercially available product are summarized in Table 1. For the measurement of ²³⁸U and ²³²Th, 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 ²²⁶Ra. However, the sensitivity for ²²⁶Ra of the previous method with the molecular recognition resin “AnaLig-Ra01” was on the 1-mBq level [15]. In addition, the recovery rate of ²²⁶Ra with the previous method was $81 \pm 4\%$ 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 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 ²²⁶Ra in Gd₂(SO₄)₃·8H₂O.

2. Experimental equipment

2.1. Chemical equipment

An “Empore Radium Rad Disk” [3] was used for chemical extraction. 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.¹ 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 volume of 800 mL (Advantech Toyo Ltd. [16], KP-47), and the holder was connected to a vacuum container (Advantech Toyo Ltd. [16], VT-500). The solution passes through the disk, and ²²⁶Ra in the solution is adsorbed by the resin bedded to the disk. The concentration of ²²⁶Ra 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 (HNO₃) (Wako Pure Chemical Industries Ltd. [17]) was used to wash the disk and efficiently dissolve Gd₂(SO₄)₃·8H₂O in the SK water.

To check the concentration of ²²⁶Ra in Gd₂(SO₄)₃·8H₂O easily, ²²⁶Ra-rich hot spring water from the Kawakita hot spring in Ishikawa, Japan [18] was used as the calibration solution. The concentration of ²²⁶Ra 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

¹ This is generally called “disk” and simply called disk in this paper from now on.

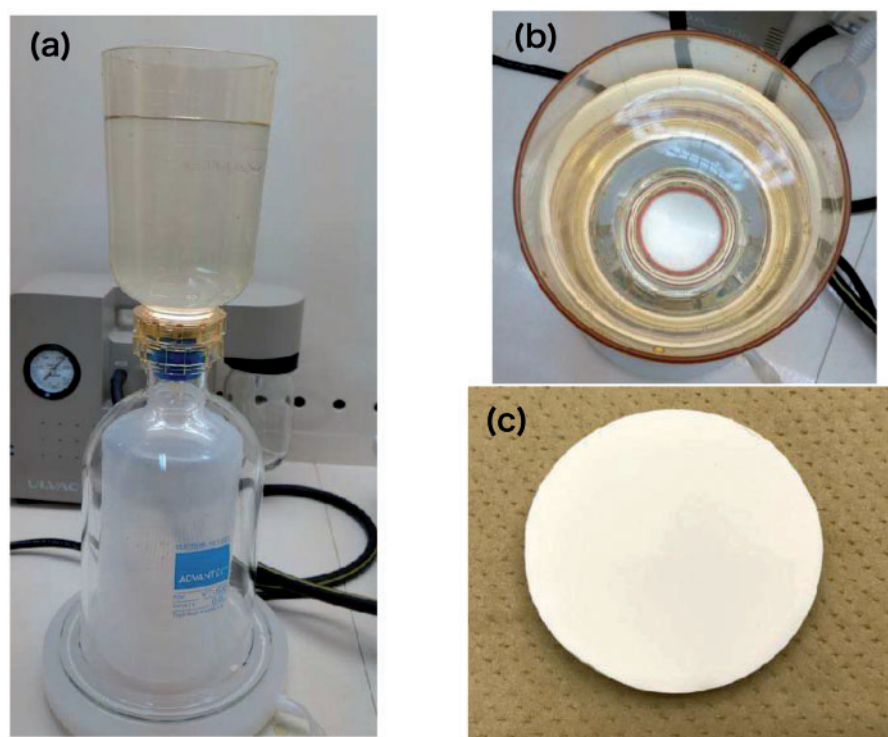


Fig. 1. (a) Photograph of the entire experimental setup. (b) Top view of the setup. (c) Top view of the disk (47 mm diameter).

HPGe detector (+30% or -10%) and statistics [15]. The sampled hot spring water was filtrated by membrane filters with pore size of $0.45\ \mu\text{m}$ and acidified to $\text{pH} \simeq 1$ 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 [19]. Thus, $1000\ \text{mg L}^{-1}$ Ba of standard solution (Merck Ltd. [20]) was used to estimate the recovery rate. The details of the recovery rate studies are described in Sect. 3. An ICP-MS “Agilent 7900” [21] 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].

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 [22]. The dimension of sample chamber was $23 \times 23 \times 48\ \text{cm}^3$. The details of the performance of the HPGe detector are described in Ref. [15]. 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 γ -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 a Monte Carlo simulation [23]. 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-rays for ^{226}Ra was determined to be 0.8% for the direct measurement

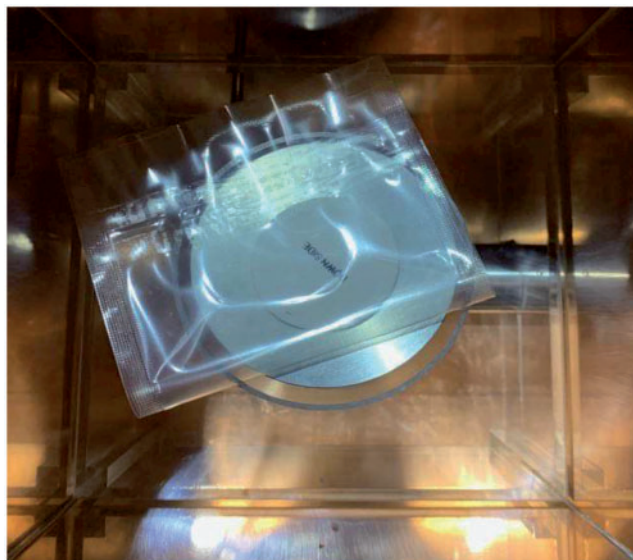


Fig. 2. Setup for the disk measurement with the HPGe detector.

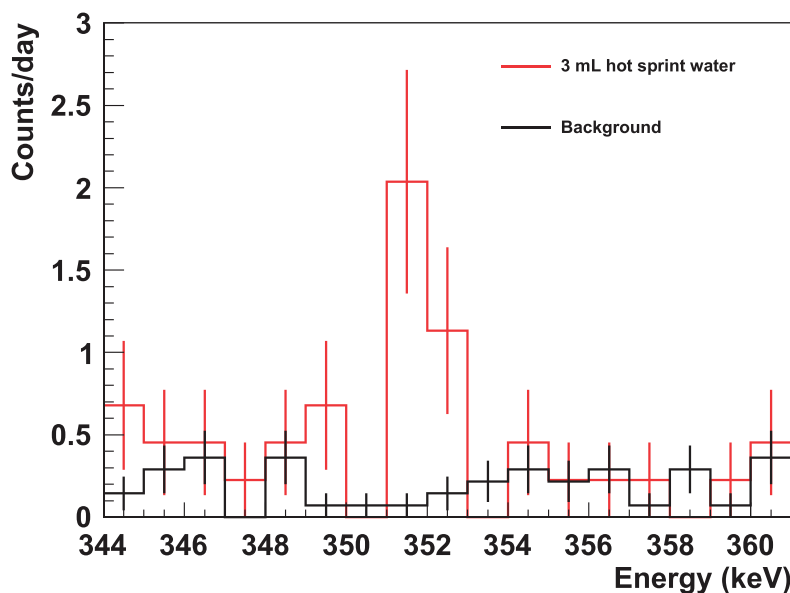


Fig. 3. Energy spectra obtained by the HPGe detector around ^{214}Bi 352 keV. The black line shows the background and the red line indicates the extracted ^{226}Ra from 3 mL of hot spring water (corresponding to 0.33 mBq). The error bar at each bin represents only statistical uncertainty.

of 5 kg of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ 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.

3. Chemical extraction of ^{226}Ra from $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ 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 $3 \text{ mol L}^{-1} \text{ HNO}_3$ and 50 mL of the ultra-pure SK water into the holder. A total of 500 g $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ was dissolved in 10 L of a $0.2 \text{ mol L}^{-1} \text{ HNO}_3$ 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 hr^{-1}). The processing time

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 | $0.33^{+0.10}_{-0.04}$ | 0.4 ± 0.2 |
| 100 | $11.2^{+3.4}_{-1.2}$ | $11.3^{+3.4}_{-1.1}$ |

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 |

for the developed method is three times faster than that used in the previous method [15] because the batch method was used in the previous study and it needed more than one hour to collect ^{226}Ra with recovery rate $> 80\%$. Compared with the batch method, the vacuum filtration method is more efficient since the sample solution directly passes through the resin bedded to the disk. Then, the disk was directly placed on the HPGe detector and measured.

In the previous method [15], the amount of ^{226}Ra for the procedure blank was estimated to be 0.3 ± 0.2 mBq by measuring 2.0 g of the resin “AnaLig-Ra01”. For a more accurate estimate of the blank amount of ^{226}Ra in the disk, a lot of disks (17 disks) were measured using the HPGe detector and the value of $1.9^{+0.6}_{-0.4}$ mBq was obtained for the 17 disks (corresponding to $0.11^{+0.04}_{-0.02}$ mBq for each disk). Therefore, the value of the blank was more precisely estimated and the detection limit was also improved.

The recovery rate of this procedure was evaluated using the ^{226}Ra -rich hot spring water. A volume of 3 mL and 100 mL of the hot spring water was added to 10 L of a $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ dissolved sample solution. Then, the concentration of ^{226}Ra adsorbed by the disk was measured using the HPGe detector for 4.5 d. As shown in Table 2, the results of the measurements were consistent with the expected amount of ^{226}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, a Ba standard solution was added to the sample solution. The sample solution with the concentration of 4.0×10^{-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 ($\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$) did not interfere with the extraction of ^{226}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 ($81 \pm 4\%$) [15].

Table 3 shows the comparison of performance between the previous method in Ref. [15] and the developed method in this study. The sensitivity of the improved method is on the 10^{-1} mBq level owing to the improvements shown in Table 3 and sufficient for measuring the experimentally allowed level of ^{226}Ra for SK-Gd.

Table 4. Summary of the measurements of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. The upper limits represent 90% confidence level.

| Lot No. | Concentration of ^{226}Ra (mBq kg^{-1}) | Measurement time (d) |
|---------|---|-------------------------|
| 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 |

4. Application to SK-Gd and results of measuring $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

SK-Gd will be conducted in several experimental phases. For the first experimental phase, 13 tons of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ will be dissolved in the SK tank corresponding to a 50% neutron tagging efficiency [9]. $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ was produced with many lots: thus, all the lots should be measured before loading. Currently, 14 tons of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ 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 $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ (unit: mBq kg^{-1}) can be obtained from the amount of ^{226}Ra measured in the disk divided by the weight of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. Table 4 shows the results of the measurement of ^{226}Ra in $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ 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 [24].

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 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 $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. Currently, all the measured $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ products, which will actually be loaded into the SK tank, were confirmed to be below the maximum allowed ^{226}Ra concentration level.

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