

Development of a method for measuring rare earth elements in the environment for future experiments with gadolinium-loaded detectors

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Demand to use gadolinium (Gd) in detectors is increasing in the field of elementary particle physics, especially in neutrino measurements and dark matter searches. Large amounts of Gd are used in these experiments. To assess the impact of Gd on the environment it is becoming important to measure the baseline concentrations of Gd. Such measurement, however, is not easy due to interference by other elements. In this paper a method for measuring the concentrations of rare earth elements, including Gd, is proposed. In the method, inductively coupled plasma-mass spectrometry is utilized after collecting the dissolved elements in chelating resin. Results of the ability to detect anomalous concentrations of rare earth elements in river water samples in the Kamioka and Toyama areas are also reported.
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1. Introduction

1.1. Gadolinium-loaded detectors

The rare earth element gadolinium (Gd) has one of the largest thermal neutron capture cross sections. Once a neutron is captured by Gd, it emits multiple γ -rays with a total energy of about 8 MeV [1]. These γ -rays can be used as signals to detect a capture event; therefore, Gd is often included in neutrino detectors. For example, the RENO experiment [2], the Double Chooz experiment [3], and the Daya Bay experiment [4], measuring the neutrino mixing matrix parameter θ_{13} , use Gd-loaded liquid scintillators to detect neutrons from inverse beta decay of reactor neutrinos ($\bar{\nu}_e + p \rightarrow e^+ + n$).

Many projects using Gd-loaded water Cherenkov detectors are currently in development. For example, the Super-Kamiokande Gd (SK-Gd) project aims to detect supernova relic neutrinos by loading Gd into the Super-Kamiokande (SK) [5] water Cherenkov detector [1]. Additionally, WATCHMAN [6] and ANNIE [7] use Gd-loaded water Cherenkov detectors. Among dark matter experiments, the XENON-1T detector will be upgraded to the XENON-nT detector with a neutron veto system based on a Gd-loaded water Cherenkov detector [8]. As applications of Gd are getting wider, particularly in physics research, it is becoming more important to accurately measure Gd in the environment

from the viewpoints of keeping the concentration of Gd constant in the detector and of preventing Gd leakage into the environment.

1.2. Surveys of anomalies of rare earth elements using ICP-MS

The concentrations of rare earth elements including Gd depend highly on substances suspended in natural water. Additionally, the concentrations of rare earth elements generally show zigzag patterns that follow the Odd–Harkins rule [9]. Therefore, to detect possible anomalies of rare earth elements in the environment, the concentrations of all rare earth elements should be measured. To minimize the effects of suspended substances and the zigzag concentrations of rare earth elements, the concentration of each rare earth element is often normalized to the concentration of chondrites (stony meteorites) [10]. The normalized concentrations of rare earth elements tend to be distributed as a smooth curve, and deviations from this smooth curve will indicate anomalies of rare earth elements.

Inductively coupled plasma-mass spectrometry (ICP-MS) is used widely to detect small amounts of elements in solutions thanks to its sensitivity. The general sensitivity of ICP-MS to rare earth elements¹ is $< 0.1 \text{ pg mL}^{-1}$. The concentrations of rare earth elements in natural water are expected to be $1\text{--}10 \text{ pg mL}^{-1}$, so ICP-MS is well suited for detecting anomalies. However, alkali metals, e.g. cesium (Cs), and alkaline earth metals, e.g. barium (Ba), are also dissolved in natural water at higher concentrations than rare earth elements. These elements can form polyatomic ions, such as barium oxide (BaO), and the concentrations of rare earth elements will tend to be overestimated when their masses are similar. This interference is generally referred to as spectral interference. To minimize spectral interference and determine the concentrations of rare earth elements precisely, we have developed a chemical separation and preconcentration procedure. As a test case, rare earth elements in the rivers of the Kamioka and Toyama areas of Japan were measured using the developed method. Details of the measurement methods and results are reported in the following sections.

2. Instrument, experimental equipment, and reagents

An Agilent 7900 was used to detect rare earth elements [11]. This ICP-MS instrument was housed in a clean room in the Kamioka mine.

To minimize spectral interference from alkali metals and alkaline earth metals and enhance the sensitivity of the ICP-MS measurements, chemical separation and preconcentration with chelating resin is often used (see, e.g., Refs. [12–14]). The MetaSEP IC-ME chelating resin was used in the experiments (GL Sciences Inc. [15]). At $\text{pH} \simeq 5$, rare earth elements are strongly adsorbed by the resin while alkali metals and alkaline earth metals are not. Figure 1 shows a schematic of the experimental setup. A column with a volume of about 20 mL and an inside diameter of 9 mm (LSC- \varnothing 9, GL Sciences Inc. [15]) was used. A valve was added at the bottom end of the column to adjust the flow rate. This setup was connected to a tip, and fixed to a free-fall manifold. The resin was sandwiched between two flits to fix it.

To produce solutions with low contamination, ultra-pure SK water [5] and ultra-high-purity analytical grade 68% nitric acid (HNO_3 , TAMAPURE AA-100 from Tama Chemicals [16]) were used. The reagents for adjusting the pH of the sample solutions were ultra-high-purity analytical grade 30% acetic acid (CH_3COOH , TAMAPURE AA-100, Tama Chemicals [16]) and 20% ammonia solution (NH_3 , TAMAPURE AA-100, Tama Chemicals [16]). The ICP-MS was calibrated and the

¹ The element promethium (Pm) is also classified as a rare earth element, but could not be determined by ICP-MS since all of its isotopes are radioactive with short lifetimes.

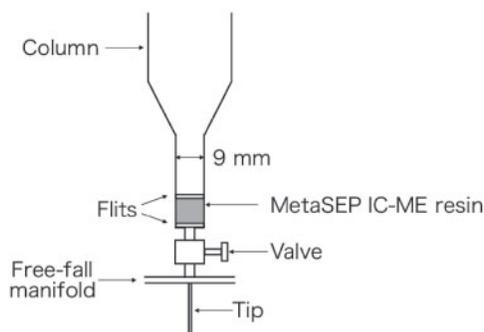


Fig. 1. Schematic of the experimental setup.

recovery rate of rare earth elements was estimated using a standard solution of 16 high-purity rare earth elements (XSTC-1, SPEX Inc. [17]). A high-purity 29-element standard solution (XSTC-331, SPEX Inc. [17]) was also used to test the recovery. Electronic (EL) grade 70% HNO_3 (Wako Pure Chemical Industries Ltd. [18]) was used to prewash the experimental equipment.

To minimize the undissolved particles in the river water, a membrane filter with pore size $0.45 \mu\text{m}$ (Omnipore filter, Merck Millipore Inc. [19]) was used. All the bottles used for collection of river water, production of the solutions, preservation of the samples, and ICP-MS measurements were made of polypropylene.

3. Experimental method

3.1. Sampling and pretreatment

On November 15 and 16, 2018 river samples were taken from upstream in the Takahara river to downstream in the Jinzu river, and from the Atotsu river in which the SK area's water flows. The sampling points are marked in Fig. 2.

River water was collected in bottles after they were washed with 1 mol L^{-1} HNO_3 (EL grade) solution and rinsed with ultra-pure SK water. The collected samples were immediately filtered using membrane filters and acidified to $\text{pH} \approx 1$ by HNO_3 , and were stored in the clean room until testing.

3.2. Chemical separation and preconcentration procedure

The resin and equipment were likely contaminated during the production process. Thus, all the equipment was soaked in 1 mol L^{-1} HNO_3 (EL grade) solution for at least one night and rinsed using the ultra-pure SK water before use.

A 0.3 g piece of the resin was loaded into the column and was set as illustrated in Fig. 1. To wash the resin, the inside of the column, the valve, and the tip, 20 mL of 3 mol L^{-1} HNO_3 (EL grade) was loaded into the column and extracted through the tip. This procedure was repeated three times. Then, 20 mL of 3 mol L^{-1} HNO_3 was loaded into the column and passed through the resin for a reference sample.

The pH of the sampled river water was adjusted to ~ 5 using CH_3COOH and NH_3 solutions. The resin was conditioned using 20 mL of the conditioning solution with $\text{pH} \approx 5$, which was made of the ultra-pure SK water, HNO_3 , CH_3COOH , and NH_3 solutions. Then, 50 mL of the sample solution was loaded into the column. The flow rate was adjusted to about 0.5 mL min^{-1} using the valve. With this procedure, most of the rare earth elements are adsorbed by the resin while the alkali metals and alkaline earth metals pass through the resin.

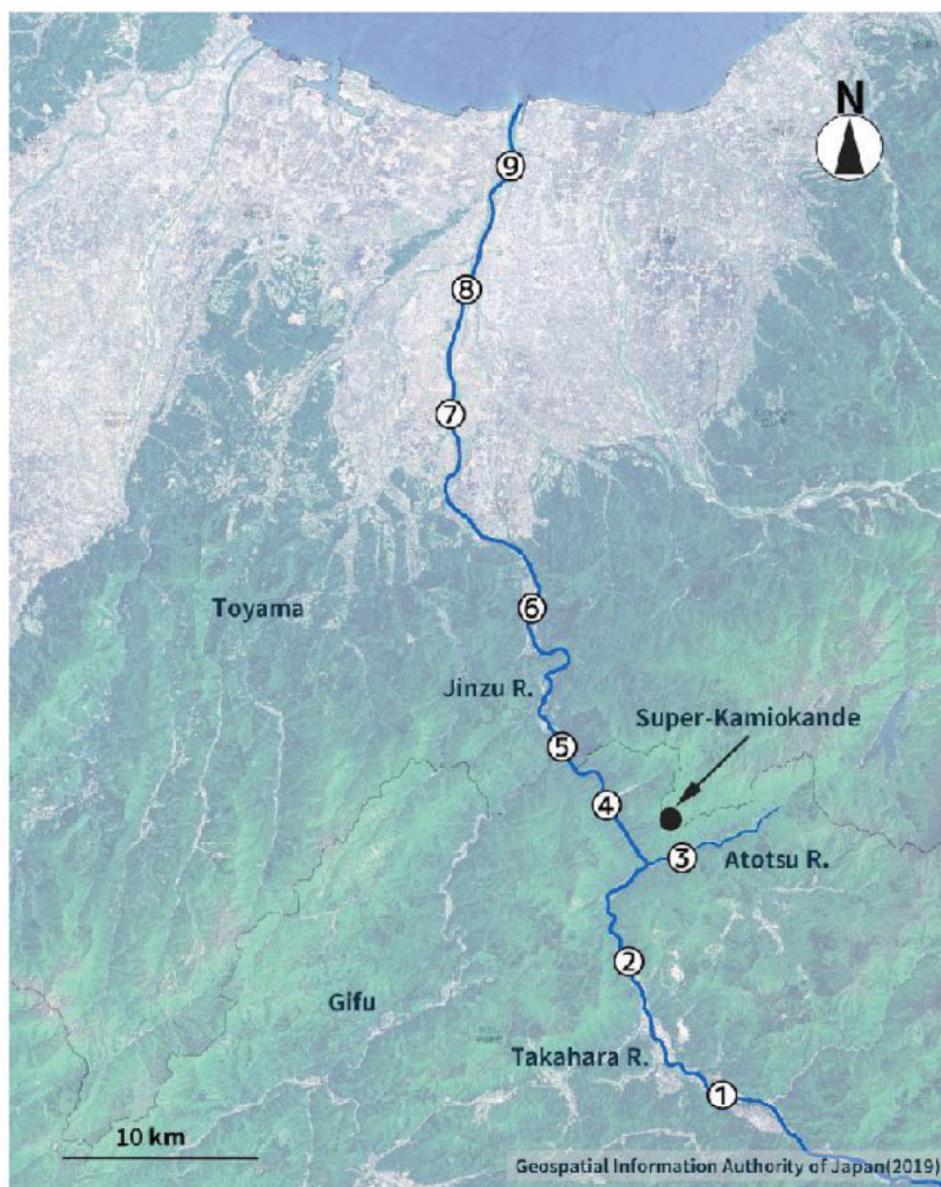


Fig. 2. Map of the sampling points [20]. For the sake of visibility, the size of the river is illustrated as larger than its actual size.

To rinse any remaining alkali metals and alkaline earth metals out of the resin, 20 mL of the conditioning solution was loaded into the column. The adsorbed rare earth elements were eluted using 10 mL of $3 \text{ mol L}^{-1} \text{ HNO}_3$ solution. All rare earth elements are concentrated by approximately a factor of five through this eluting procedure. The eluted solution was collected and measured with the ICP-MS. The total time for the chemical separation and preconcentration procedure and the ICP-MS measurement was about one day.

4. Results and discussions

Before measurement of the river water samples, the recovery rates of rare earth elements were evaluated using 10 pg mL^{-1} XSTC-1 and 10 ng mL^{-1} XSTC-331 solutions. Figure 3 shows the

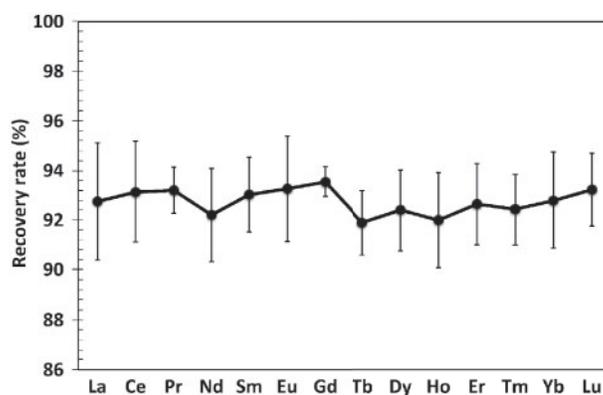


Fig. 3. Evaluated recovery rates of all rare earth elements measured using XSTC-1 solution.

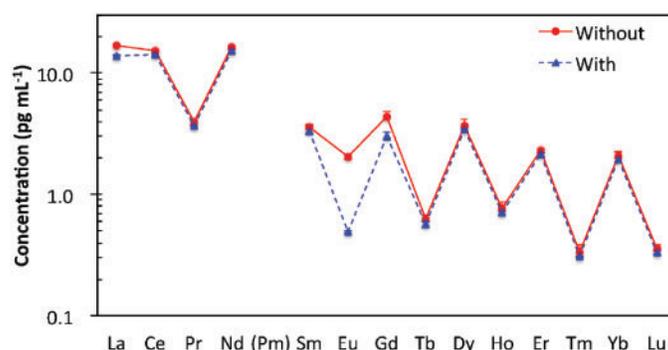


Fig. 4. Comparison of sample 1 between the measurements with (red circles with solid red line) and without (blue triangles with dashed blue line) the developed chemical separation and preconcentration procedure. The errors are small enough and the illustrated error bars are too small to be visible.

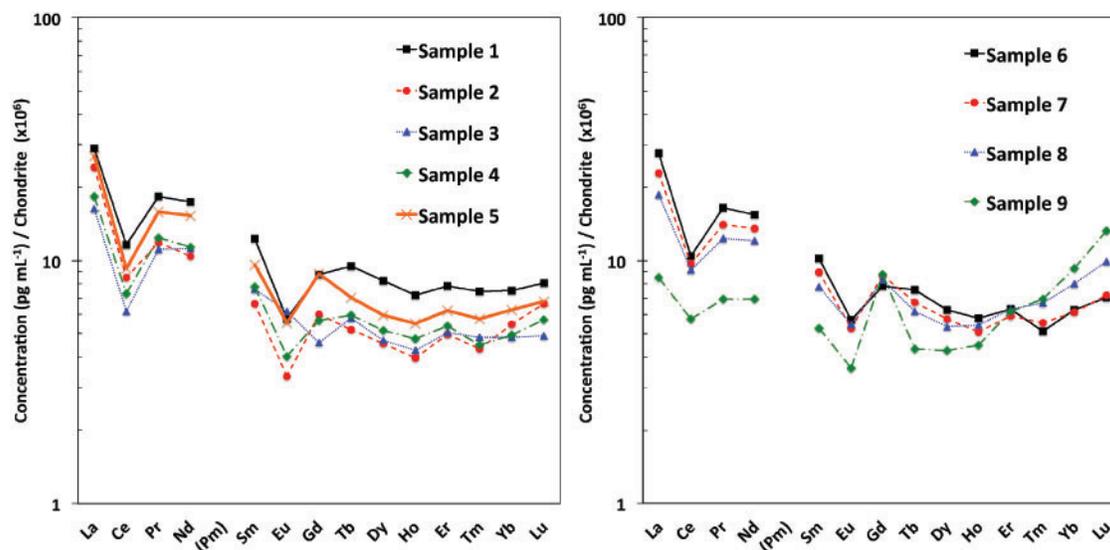
recovery rates of all rare earth elements. All were recovered to $> 90\%$, while alkali metals and alkaline earth metals like Cs and Ba were eliminated to $< 0.1\%$.

Figure 4 shows a comparison of results from sample 1 when it was prepared with and without the chemical separation and preconcentration procedure. Typical spectral interference is shown in europium (Eu). The concentration of Eu as measured with ^{153}Eu without any chemical separation or preconcentration procedure was 2.0 pg mL^{-1} , while the concentration determined with the developed method was 0.5 pg mL^{-1} . This gap is explained by spectral interference from $^{137}\text{Ba}^{16}\text{O}$. The concentrations of lanthanum (La) and Gd in the direct measurements were $16.9 \pm 0.2 \text{ pg mL}^{-1}$ and $4.4 \pm 0.5 \text{ pg mL}^{-1}$, respectively. These values are also higher than the results found with the developed chemical separation and preconcentration procedure ($14.0 \pm 0.3 \text{ pg mL}^{-1}$ for La and $3.0 \pm 0.2 \text{ pg mL}^{-1}$ for Gd, respectively). These gaps also imply the possibility of spectral interference in La and Gd measurements. If the sample solutions are directly measured by the ICP-MS without any chemical extraction and preconcentration procedure, the elements may be overestimated due to significant spectral interference. On the other hand, the spectral interference for rare earth elements can be efficiently minimized using the developed method.

Table 1 lists the results of the measurements of rare earth elements in the river waters using the developed method. For the concentrations of rare earth elements, the values of the blanks were subtracted and the recovery rate was corrected. Figure 5 shows the concentrations of rare earth elements in all samples normalized to chondrite concentration. The normalized concentrations should

Table 1. Measurements of the river samples (unit: pg mL^{-1}). Values without error had the negligible error.

	Sample								
	1	2	3	4	5	6	7	8	9
La	14.0±0.3	11.7±0.5	7.9±0.2	8.9±0.5	13.1±0.3	13.4±0.5	11.1±0.3	9.0±0.5	4.1±0.2
Ce	14.3±0.4	10.5±0.5	7.6±0.2	9.0±0.4	11.4±0.3	12.8±0.6	11.9±0.4	11.3±0.5	7.0±0.3
Pr	3.7	2.4	2.2±0.1	2.5±0.1	3.2	3.3±0.1	2.8	2.5±0.1	1.4±0.1
Nd	15.3±0.6	9.2±0.4	9.8±0.2	10.0±0.8	13.5±0.3	13.5±1.0	11.9±0.3	10.6±0.4	6.1±0.1
Sm	3.4±0.3	1.8±0.1	2.1±0.1	2.1±0.1	2.6±0.1	2.8±0.2	2.4±0.1	2.1	1.4±0.1
Eu	0.5	0.3	0.5	0.3	0.5	0.5	0.5	0.5	0.3
Gd	3.0±0.2	2.1±0.2	1.6±0.2	2.0±0.3	3.0±0.2	2.7±0.2	3.0±0.3	2.9±0.2	3.0±0.2
Tb	0.6	0.3	0.3	0.4	0.4	0.5	0.4	0.4	0.3
Dy	3.4±0.1	1.9±0.1	1.9±0.1	2.1±0.1	2.5±0.1	2.6±0.1	2.4±0.1	2.2±0.2	1.8±0.1
Ho	0.7	0.4	0.4	0.5	0.5	0.6	0.5	0.5	0.4
Er	2.1±0.1	1.4	1.4±0.1	1.5±0.1	1.7	1.7±0.2	1.6±0.1	1.7±0.1	1.7±0.1
Tm	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.3
Yb	1.9±0.1	1.4±0.1	1.3±0.1	1.3±0.1	1.6±0.1	1.6±0.2	1.6±0.1	2.1±0.2	2.4±0.1
Lu	0.3	0.3	0.2	0.2	0.3	0.3	0.3	0.4	0.5

**Fig. 5.** Normalized concentrations of rare earth elements in samples 1 to 5 (left) and samples 6 to 9 (right).

be distributed on a smooth curve since the natural zigzag pattern of rare earth elements is minimized by the normalization. However, negative anomalies for cerium (Ce) and Eu can also be seen in all samples except for sample 3. Those anomalies are caused by different oxidation rates. The valence of all rare earth elements is usually +3; however, Ce and Eu can have two different valences, +3 and +4 for Ce and +2 and +3 for Eu, under different redox conditions. Ions of Ce^{4+} and Eu^{2+} are more easily oxidized, resulting in the negative anomalies.

A positive anomaly for Gd can be seen in sample 9. Because compounds of Gd are used widely as a contrast medium for magnetic resonance imaging in medical diagnostics, it is often observed in urban regions [21,22].

All rare earth elements can be detected using the developed method, and no anomalous concentrations of rare earth elements were found near SK. After normalization, the concentration of each rare

earth element can be compared and the excess of rare earth elements can be examined. Therefore, this method is appropriate for assessing the concentration of Gd in the environment.

5. Conclusion

New experiments that use Cherenkov detectors with Gd-loaded water are in development. A method for the assessment of Gd in the environment has been established with the chemical separation and preconcentration procedure described above. This procedure eliminates spectrum interference in ICP-MS measurements from alkali metals and alkaline earth metals, while retaining more than 90% of all the rare earth elements. Consequently, all rare earth elements, including Gd, can be determined with a precision of 0.1 pg mL^{-1} . This concentration corresponds to about 1 g d^{-1} of Gd leakage from the SK tank to the environment.

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