Rapid analysis of ^{226}Ra in ultrapure gadolinium sulfate octahydrate

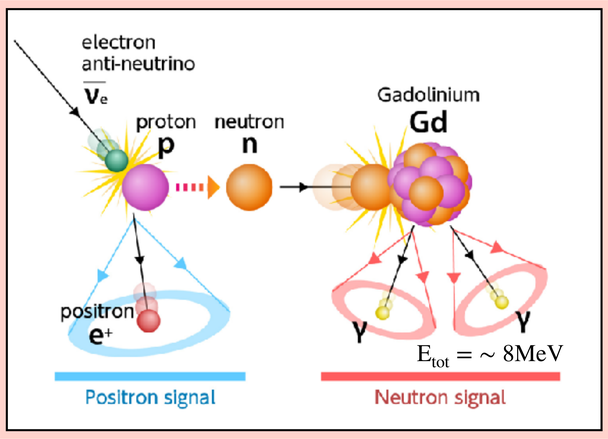
PTEP 103H01(2023), https://doi.org/10.1093/ptep/ptad117

Kamioka Observatory, ICRR
The University of Tokyo

Keishi Hosokawa

hosokawa@km.icrr.u-tokyo.ac.jp

Introduction



- Gadolinium(Gd)
  - the most significant thermal neutron capture cross-section among all elements.
  - E_{tot} = ~ 8MeV
- Numerous experiments utilize Gd to detect anti-neutrinos via inverse beta decays or to remove neutron induced BG.

- To load Gd into water Cherenkov detectors, $Gd_2(SO_4)_3 \cdot 8H_2O$ is dissolved.
- Rare search experiments are required to screen for radioactive impurities in $Gd_2(SO_4)_3 \cdot 8H_2O$ before dissolution.
- This method requires only 3 days to measure a batch of samples, as opposed to the usual method using high-purity germanium(HPGe) detectors, which takes ~20 days after arrival.

Isotope	Natural abundance ratio [%]	Thermal capture cross section [barn]
^{152}Gd	0.20	740
^{154}Gd	2.18	85.8
^{155}Gd	14.80	61100
^{156}Gd	20.47	1.81
^{157}Gd	15.65	254000
^{158}Gd	24.84	2.22
^{160}Gd	21.86	1.42
^{1}H	99.99	0.33
^{16}O	99.76	0.0002
^{32}S	94.85	0.53

Method and its performance

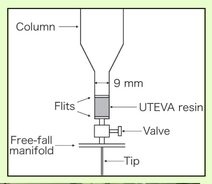
Chemical separation

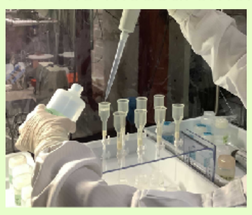
- Various measurements are possible by combinations of chemicals, detectors, etc.

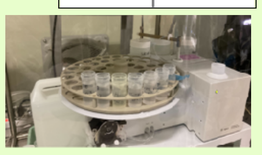
Example 1:

Applied in SK-Gd — https://doi.org/10.1093/ptep/ptx145

U/Th extraction from Gd sulfate using UTEVA resin
↓
ICP-MS measurement





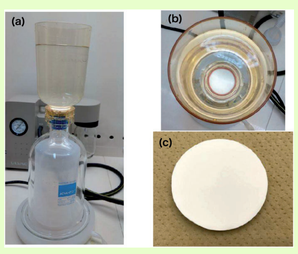


	U (pg mL^{-1}) ICP-MS measurement	U (mBq/kg) Converted to powder	Th (pg mL^{-1}) ICP-MS measurement	Th (mBq/kg) Converted to powder
Sample A	0.02 ± 0.01	< 0.04	0.15 ± 0.01	0.06 ± 0.01
Sample B	0.04 ± 0.01	0.05 ± 0.01	0.30 ± 0.01	0.12 ± 0.02
Sample C	0.52 ± 0.01	0.64 ± 0.10	4.35 ± 0.18	1.77 ± 0.27
Procedure blank	0.01	—	0.01	—
Commercial[a]	0.23	28±2	0.47	19 ± 1
Requirement	—	5	—	0.05

Example 2:

Applied in SK, HK — https://doi.org/10.1093/ptep/ptaa105

^{226}Ra extraction using disk-shaped AnaLig Ra-01 resin, Empore Radium Rad Disk.
↓
HPGe measurement



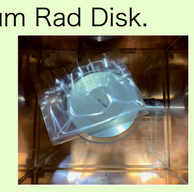
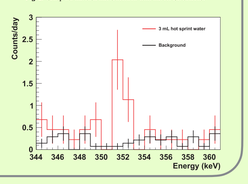
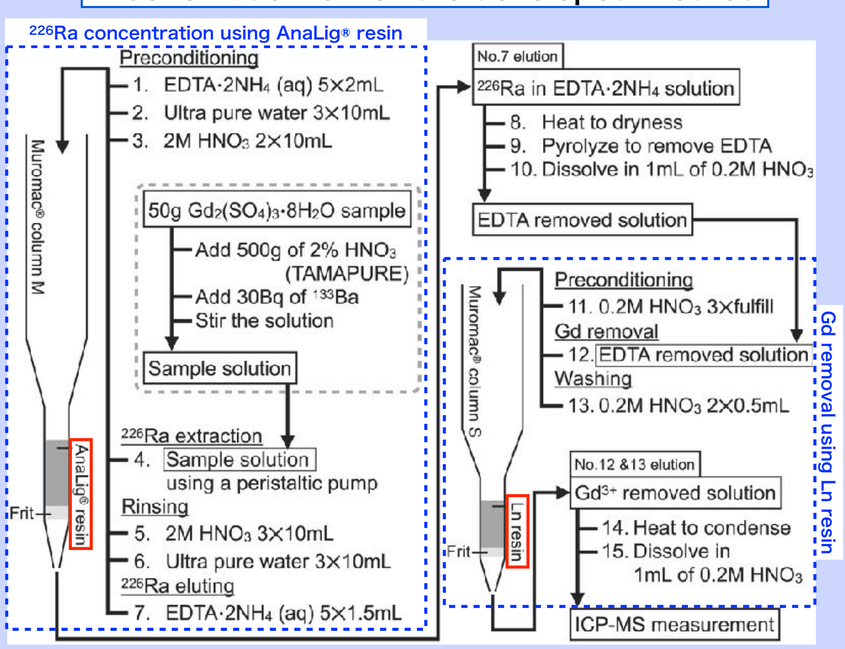


Fig. 2. Setup for the disk measurement with the HPGe detector.



Experimental method

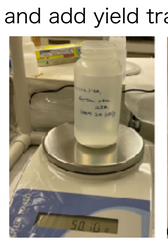
A Schematic view of the developed method

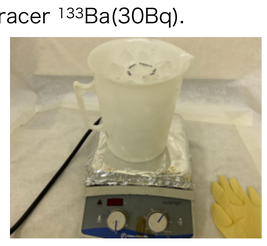


Photographs of the measurements

1. Sample solution preparation

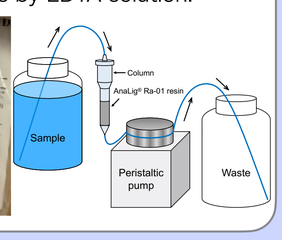
Solve 50g Gd sulfate into 500g 2M HNO_3 and add yield tracer ^{133}Ba(30Bq).





2. Chemical separation of ^{226}Ra

Extract Ra ions using AnaLig® Ra-01. Elute Ra ions by EDTA solution.



Struggling to measure ^{226}Ra by ICP-MS

Example 1 at left

Short half-life

Since ^{226}Ra half-life is short(1600y),

$$1\ \mathrm{Bq}\ (^{238}\mathrm{U}) = 8.0 \times 10^{-5}\ \mathrm{g}$$
$$1\ \mathrm{Bq}\ (^{226}\mathrm{Ra}) = 2.7 \times 10^{-11}\ \mathrm{g}$$

6-order improvement of the sensitivity is required when comparing the same intensity ^{238}U.

Increasing the enrichment ratio

2g sample in ^{238}U measurement
$\xrightarrow{\times 25}$ 50g sample in this work
Amount of the eluent 18mL $\xrightarrow{\times 18}$ 1mL

Procedure Blank

Clean environment, reagents, containers, etc.

^{238}U measurement: ~10×10^{-15} g/mL
This work: 0.2×10^{-15} g/mL $\downarrow \times \frac{1}{50}$

ICP-MS improvement

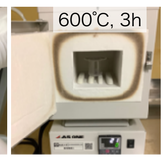
A solvent removal module, Aridus II is installed. It minimizes sample loss at the ICP-MS injector and prevents a drop in plasma temperature. In addition, several optimization is performed.

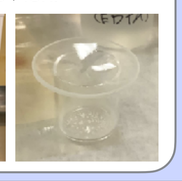
ICP-MS Detection limit

^{238}U measurement: 13×10^{-15} g/mL
$\downarrow \times$ ~ 1/200
This work: 0.06×10^{-15} g/mL

3. EDTA pyrolysis

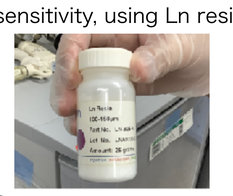
Impurities in the eluent could decrease the sensitivity of the ICP-MS. It is necessary to decompose the EDTA and SO_4 ion.

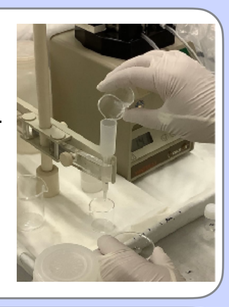




4. Gd removal

Remove Gd^{3+} ions which also could decrease the sensitivity, using Ln resin.





5. ICP-MS measurement (after ^{133}Ba recovery rate measurement by HPGe)

About 1 mL of eluent is measured using ICP-MS. The standard addition method is adopted.

Performance

	^{226}Ra amount in eluent(fg/g)	Eluent amount (g)	^{226}Ra contamination (μBq)	^{133}Ba recovery rate (%)
Procedure Blank 1	0.24±0.01	1.00	8.8±0.3	48.2±2.4
Procedure Blank 2	0.13±0.01	1.03	4.9±0.1	46.5±2.5
Procedure Blank 3	0.19±0.01	1.09	7.4±0.2	53.2±1.8

- Procedure Blank
  - Contamination caused by containers, reagents, and environment
  - Evaluated by performing this method to non-Gd-dissolved HNO_3.
  - ^{226}Ra contamination : 7.0 ± 1.1 μBq
    - Assuming 50g $Gd_2(SO_4)_3 \cdot 8H_2O$ dissolving, this value corresponds to 0.29 ± 0.05 mBq/kg(powder).
  - The detection limit is 0.43 mBq/kg (99.73% CL).
    → This limit meets the SK-Gd requirement.
- This method takes only 3 days to process a batch of samples, including the procedure blank measurement.

Application to SK-Gd samples

	^{226}Ra amount in eluent(fg/g)	Eluent amount (g)	^{226}Ra contamination (μBq)	^{133}Ba recovery rate (%)	Sample amount (g)	^{226}Ra concentration in Gd sulfate (mBq/kg)	99.73% CL. upper limt (mBq/kg)
Procedure Blank	0.37±0.02	1.01	13.7±0.7	not measured	-	0.89±0.06 0.55±0.03	1.06 0.63
SK-Gd Sample A	0.30±0.01	1.15	12.6±0.4	30.3±1.3	50.1	0.84±0.05	0.98
SK-Gd Sample B	0.13±0.01	1.21	5.8±0.4	48.8±0.8	51.2	0.23±0.02	0.29

- The new method was applied to SK-Gd samples.
- ^{226}Ra concentration in the samples are comparable or less than the procedure blank.
  - The ^{226}Ra amounts in the samples meet the SK-Gd requirement.
- HPGe result: (A)<0.46, (B)<0.60 mBq/kg

SK-Gd requirement for Gd sulfate

Table 1: Criteria of radioactive impurities in $Gd_2(SO_4)_3 \cdot 8H_2O$ powder.

Chain	Isotope	Criterion [mBq/kg]	Physics target
^{238}U	^{238}U	< 5	SRN
	^{226}Ra	< 0.5	Solar
^{232}Th	^{232}Th	< 0.05	Solar
	^{228}Ra	< 0.05	Solar
^{235}U	^{235}U	< 30	Solar
	^{227}Ac/^{227}Th	< 30	Solar

Summary

- Numerous experiments utilize Gd to detect anti-ν via IBD or to remove neutron BG.
- HPGe measurements for $Gd_2(SO_4)_3 \cdot 8H_2O$ takes ~20 days after arrival.
- This study developed a new method to rapidly measure the ^{226}Ra concentration in $Gd_2(SO_4)_3 \cdot 8H_2O$.
  - This method requires only 3days to measure a batch of samples.
  - Procedure blank : 0.29 ± 0.05 mBq/kg
  - Detection limit : 0.43 mBq/kg (99.73% CL)
- The method was applied to two $Gd_2(SO_4)_3 \cdot 8H_2O$ samples from SK-Gd. It was found that the amount of ^{226}Ra in the samples is within acceptable limits for continuing ^{8}B solar neutrino measurements in SK-Gd.
- This study can be used where a rapid evaluation of 226Ra in $Gd_2(SO_4)_3 \cdot 8H_2O$ is required.