

Special features of the new thermal ionization mass spectrometer installed at the National Museum of Nature and Science, and their precision, reproducibility and long term stability on isotopic ratio measurements

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Abstract A new thermal ionization mass spectrometer, Thermo Fisher Scientific TRITON plus, was installed at the Department of Science and Engineering, Tsukuba research departments, National Museum of Nature and Science (NMNS) on October 2011. The mass spectrometer is equipped with 9 Faraday cups and 1 Secondary Electron Multiplier (SEM) on its detector system. It is also equipped with “L5 platform” at the low mass region of the L4 Faraday cup, which enables high sensitive measurements for Ba and Nd isotopic ratios with 3 Compact Discrete Dynode detectors (CDDs) and the center SEM. For Gd isotopic ratio measurements, 3 more CDDs are equipped on the high mass region of the H4 Faraday cup. With 12 replicate runs on Sr and Nd isotopic ratio measurements using Faraday cups, the internal precisions of 200 ratio measurements were 2.4–4.1 ppm for Sr and 2.9–3.9 ppm for Nd (1SE), and external precisions of 10 runs out of 12 were 4.0 ppm for Sr and 3.0 ppm for Nd (1SD). For more than one year from the installation, measured isotopic data of the Sr standard show the stability of 10 ppm (1SD), far more stable than the previous mass spectrometer.

Key words: thermal ionization, mass spectrometer, TRITON, precision, isotopic ratio

1. Introduction

Isotopic ratio measurements of the elements are essential for the determination of atomic weights¹⁾ and age of meteorites and rocks²⁾. Isotopic signatures are also used to trace processes which occurred inside the Earth and in the early solar nebula. Thermal ionization mass spectrometers are used for these purposes to measure pre-

cise isotopic ratios of many heavy elements such as Sr, Nd, Pb and U. Department of Science and Engineering, NMNS has long been studying isotopic ratios of the elements using a modified JEOL JMS-D300 mass spectrometer³⁾ followed by a VG Sector 54–30 thermal ionization mass spectrometer⁴⁾, and determined the atomic weight of Ti⁵⁾, age of enstatite chondrites⁶⁾, sources of Permian and Triassic cherts⁷⁾, traces

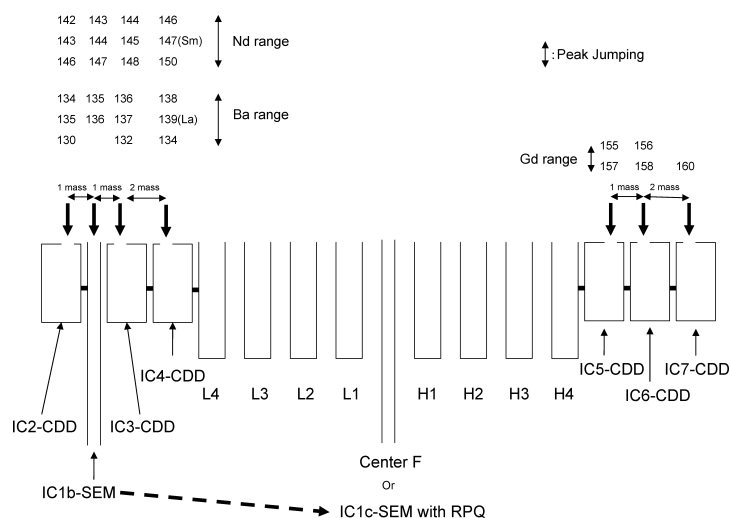


Fig. 1. A schematic diagram of the collector assemblage of the TRITON plus mass spectrometer at NMNS. 9 Faraday cups (C, L1 to L4, and H1 to H4), 1 conventional Secondary Electron Multiplier (SEM; IC1), and 6 thin type SEMs called as Compact Discrete Dynode detectors (CDDs; IC2 to IC7) are equipped.

of the extinct nuclide ^{135}Cs in chondrites⁸⁾, abundance of the natural radiogenic nuclide ^{53}Mn in an ion meteorite⁹⁾, *etc.*

Since the VG Sector 54–30 mass spectrometer was installed at the Shinjuku branch of NMNS in 1994, 17 years has passed and the performance of the mass spectrometer became degraded. NMNS decided to replace it with a new mass spectrometer, Thermo Fisher Scientific TRITON plus, on the occasion of the move of all departments in the Shinjuku branch to Tsukuba in 2011. The instrument installation started on October 3, 2011, which was delayed partly due to the earthquake, and finished on December 8, 2011. Here we report the special features of this new mass spectrometer, especially the new detectors, and their precision and reproducibility. We also discuss about the long term stability on isotopic ratio measurements in comparison with the previous mass spectrometer.

2. Detector system

A schematic diagram of the collector assemblage of the TRITON plus mass spectrometer at NMNS is shown in Fig. 1. It is equipped with 9

Faraday cups: a center cup (C) is fixed and 4 cups are placed in each side, H1 to H4 cups in the high mass side and L1 to L4 cups in the low mass side, which can be moved by motors to adjust suitable mass distances. One large Secondary Electron Multiplier (SEM), called as IC1c (IC: Ion Counter), is placed on the back of the center Faraday cup and the ion beam is switched to enter either collector by the reflection high voltage.

It is also equipped with “L5 platform” at the low mass region of the L4 Faraday cup, which enables high sensitive measurements of isotopic ratios with 3 Compact Discrete Dynode detectors (CDDs), IC2 to IC4, and the center SEM, IC1b. IC1b is the same SEM located on the back of the center Faraday cup, but the ion beam is re-routed from the L5 platform. CDDs are thin (7 mm wide) SEMs, which can be located beside the Faraday cups. The performance of CDDs are nearly comparable to the large size traditional SEM and the dynamic range of CDDs are one order of magnitude higher than the channeltron detectors. However, they occupy about twice the width of the standard Faraday cups and cannot be located every one mass distance for more than

3 masses.

For the NMNS TRITON plus, the mass distances of the collectors in the L5 platform are set suitable for the Ba and Nd isotopic measurements as shown in Fig. 1. Only the distance between IC1b and IC3 can be moved with the L4 Faraday cup. Small differences of the mass distances (up to 10%) between Ba and Nd can be adjusted electronically, called as “Zoom Optics”. For Gd isotopic ratio measurements, 3 more CDDs, IC5 to IC7, are equipped on the high mass region of the H4 Faraday cup. The ion counters can be used with the Faraday collectors. Thus, 9 major isotopes with Faraday cups and several minor isotopes with ion counters can be measured simultaneously.

3. Cup configurations and Peak shapes

Typical peak shapes of Sr and Nd ion beams with Faraday cup configurations of static measurements are shown in Fig. 2 (a) and (b), respectively. The peak plateau flatness is excellent and the decay of the peak height is less than 50 ppm at the mass of 0.02% both higher and lower from the peak center. For the Sr static measurements, the interfering ^{87}Rb is monitored by ^{85}Rb with the center Faraday cup. Also, for the Nd static measurements, the interfering ^{142}Ce is monitored by ^{140}Ce with the L4 cup. If Sm corrections are needed, ^{147}Sm is measured with H2 collector and ^{148}Nd and ^{150}Nd are measured with H3 and H4 collectors, respectively.

Typical peak shapes of Ba and Nd ion beams with L5 platform ion counters are shown in Fig. 2 (c) and (d), respectively. Although the peak plateau flatness is not as good as the Faraday cups, stable magnet field and high accelerating voltage (30 ppm for 30 min) help to keep the peak center. The dark noises were 0.2 to 3.4 cpm with more than 95% counting efficiency, which are more than 10^4 times lower than the Faraday cup amplifier noises. Since there are only 4 ion counters in the L5 platform and there is 2 mass distance between IC3 and IC4, peak jumping is necessary to measure all isotopes of Ba and Nd.

For example, at the Ba isotope measurements, IC1 is set to ^{135}Ba , then jump to ^{136}Ba , and at the last to the mass 131 for the measurements of ^{130}Ba with IC2 and ^{132}Ba with IC3.

4. Precisions and Reproducibility

Results of 12 replicate runs of isotopic ratio measurements on the Sr and Nd standard (NIST SRM 987 and GSJ JNdi-1, respectively) using Faraday cups are shown in Table 1 and Fig. 3. The internal precisions of 200 ratio measurements were 2.4–4.1 ppm for Sr and 2.9–3.9 ppm for Nd (1SE), and external precisions of 10 runs out of 12 were 4.0 ppm for Sr and 3.0 ppm for Nd (1SD). Although the certified value of NIST SRM 987 is 0.71034 ± 0.00026 , ratios between 0.71022 and 0.71026 are normally reported and our data fit in this range. Tanaka *et al.* (2000) reported that the inter-laboratory calibrated value of GSJ JNdi-1 is $0.512115 \pm 0.000007^{(10)}$, correspond to the La Jolla standard value of 0.511858. Since ratios between 0.511840 and 0.511860 are reported for the La Jolla standard, our JNdi-1 data are also in good agreement with the reported value.

5. Long term stability

The NIST SRM 987 Sr standard data measured by both Sector 54–30 and TRITON plus mass spectrometers over 17 years are plotted in Fig. 4. The Sector 54 mass spectrometer had a trouble in the detector system around 1998. The pre-amplifier boards were contaminated by oil mists from the rotary pump and the Sr standard data deviated significantly. After cleanup of the boards by isopropyl alcohol, the data seemed recovered but the internal and external errors were large. The Faraday cups were replaced to new deep type cups in 2004 and the pre-amplifier boards were also replaced in 2008, which stabilized the deviation of the Sr standard data and individual internal errors became slightly small.

Internal errors of the Sr standard data measured by the TRITON plus are so small that error

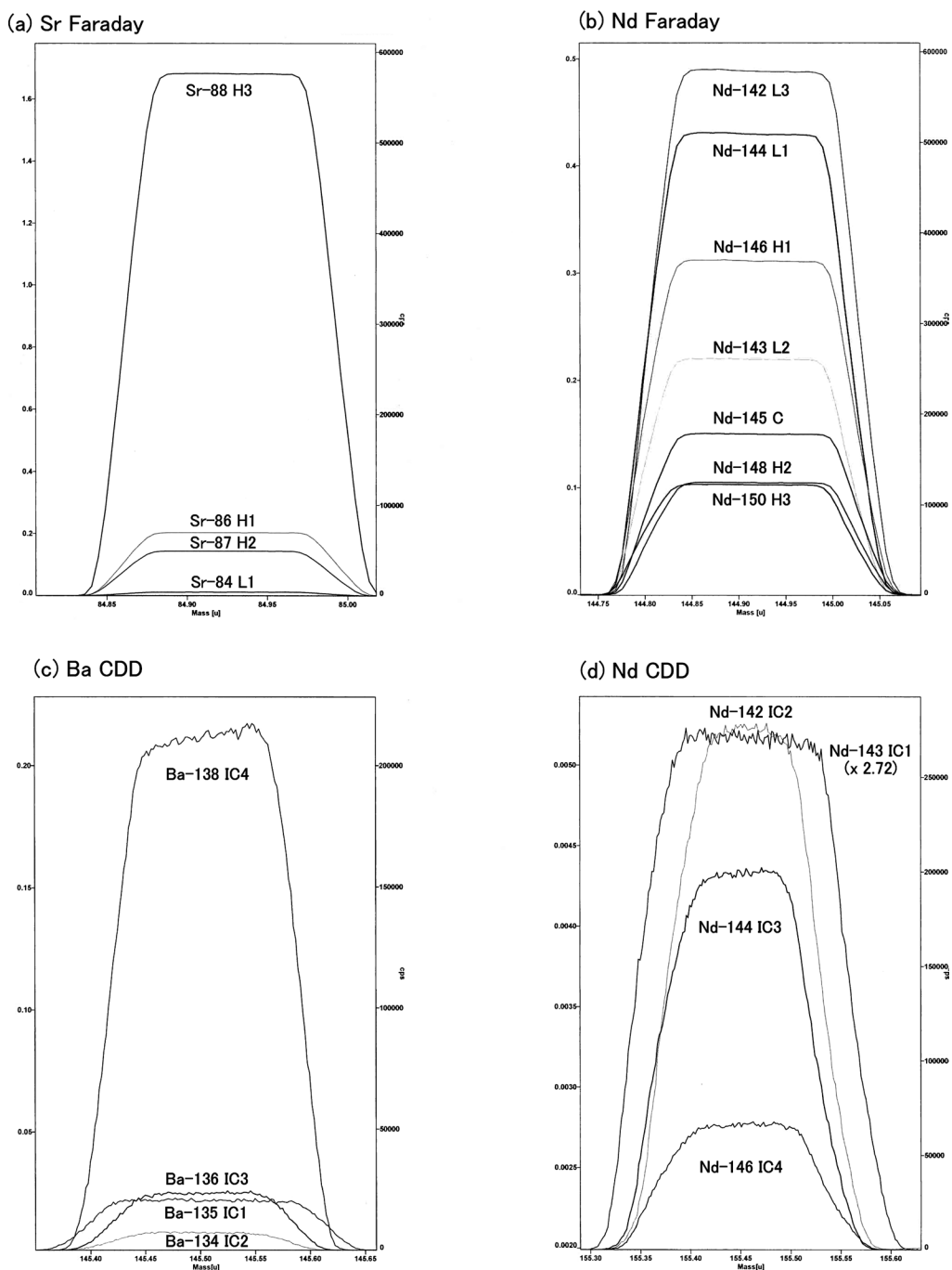


Fig. 2. Typical peak shapes of the Faraday collectors for (a) Sr and (b) Nd, and those of L5 platform ion counters for (c) Ba and (d) Nd.

bars are almost hidden by the plot symbols in Fig. 4. Plots of the data measured by the TRITON plus are blown up in the lower right corner. The

average of the TRITON plus data is 0.7102458 ± 0.0000070 (1SD), only 10ppm fluctuations over 1 year period of time.

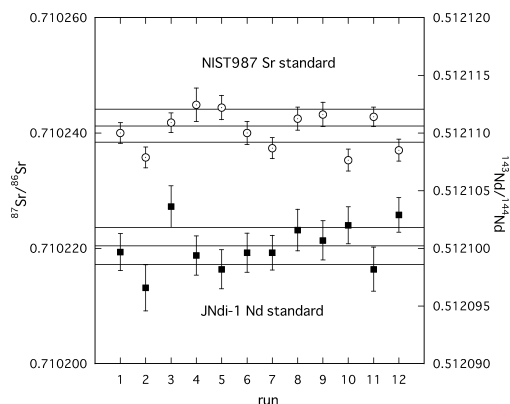


Fig. 3. Results of 12 replicate runs of isotopic ratio measurements on the Sr and Nd standard (NIST SRM 987 and GSJ JNdi-1, respectively) using Faraday cups. (Error bars are 1 sigma standard errors.)

6. Conclusion

The new thermal ionization mass spectrometer, TRITON plus, installed in NMNS is a stable, highly precise isotopic ratio determination machine. We already measured the age of unique alkali-rich fragments found in a LL chondrite⁽¹⁾ and started the researches on meteorites and terrestrial rocks. We are still trying to find appropriate ways to use the CDDs, highly sensitive detectors, but are confident that they are the powerful tool for the isotopic measurements of samples with small amounts.

Table 1. Internal and external precisions of Sr and Nd standards (NIST987 and JNdi-1) at installation of NMNS Triton plus

run	Sr-87/Sr-86	Standard Error	SE (%)	Nd-143/Nd-144	Standard Error	SE (%)
1	0.7102383	0.0000018	0.00025	0.5120997	0.0000016	0.00031
2	0.7102358	0.0000018	0.00026	0.5120966	0.0000020	0.00039
3	0.7102418	0.0000017	0.00024	0.5121036	0.0000018	0.00036
4	0.7102449	0.0000029	0.00041	0.5120994	0.0000017	0.00034
5	0.7102444	0.0000021	0.00030	0.5120982	0.0000017	0.00033
6	0.7102400	0.0000020	0.00028	0.5120996	0.0000017	0.00033
7	0.7102374	0.0000018	0.00026	0.5120996	0.0000015	0.00030
8	0.7102425	0.0000020	0.00028	0.5121016	0.0000018	0.00035
9	0.7102432	0.0000021	0.00029	0.5121007	0.0000017	0.00033
10	0.7102353	0.0000019	0.00027	0.5121020	0.0000016	0.00031
11	0.7102428	0.0000017	0.00024	0.5120982	0.0000019	0.00036
12	0.7102370	0.0000019	0.00027	0.5121029	0.0000015	0.00030
mean	0.7102412	0.0000029	0.00040	0.5121002	0.0000016	0.00030

*Shaded data are excluded from the calculation of external errors

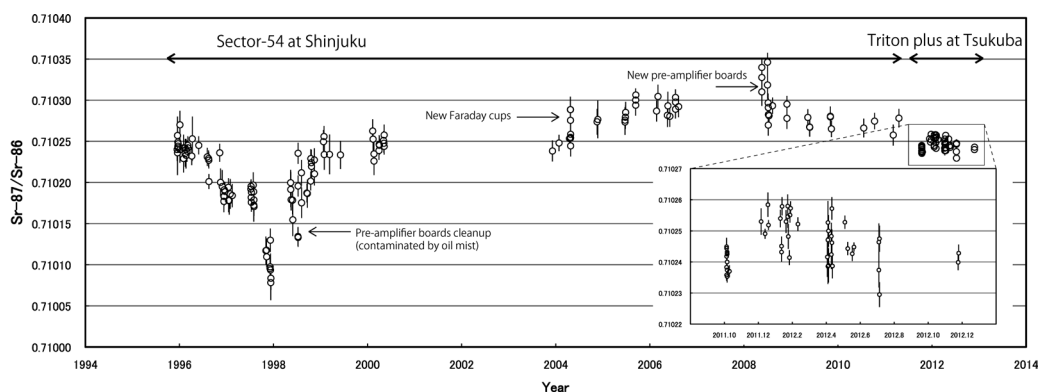


Fig. 4. The NIST SRM 987 Sr standard data measured by both Sector 54-30 and TRITON plus mass spectrometers over 17 years. Data measured by the TRITON plus are blown up in the lower right corner. (Error bars are 1 sigma standard errors.)

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