Application Note: 30158

High Precision Isotope Ratio Measurements of Sr, Nd and Hf

Key Words

- NEPTUNE
- Multicollector ICP-MS
- Hafnium
- Neodymium
- Strontium

Introduction

Multicollector-ICP-MS has been established as a routine analytical technique for high precision isotope ratio measurements of radiogenic, as well as stable isotope systems. The high sensitivity for elements with a high first ionization potential (e.g. hafnium) and the constant mass bias over time make MC-ICP-MS a very robust and reliable technique. For the analysis of the "heavy stables" (e.g. Mg, Si, Ca, Fe, Zn), high mass resolution has turned out to be a must in order to discriminate molecular interferences from the pure elemental peaks. The Thermo Scientific NEPTUNE MC-ICP-MS pioneered a new generation of MC-ICP-MS instruments, because of its capability for high mass resolution and its unique amplifier and collector system, which has proven ultimate resolution and stability on the Thermo Scientific TRITON TIMS instruments already.

The purpose of this study is to explore the achievable external reproducibility of the elements Sr, Nd and Hf on the NEPTUNE under different experimental conditions. For this purpose we used our NEPTUNE Tune solution. This solution is used during final test and during the installation acceptance in the customer's lab. It contains 1 ppm Li, 3 ppm Fe and 200 ppb Sr, Nd, Hf, Tl, Pb and U, dissolved in 3% HNO_3.

1. In a first approach, we measured Sr, Nd and Hf isotope ratios in the NEPTUNE Tune solution under wet plasma conditions using the Stable Introduction System (SIS). It consists of a double pass quartz spray chamber and a low flow PFA nebulizer.
2. In a second approach, we measured Sr, Nd and Hf isotope ratios in the NEPTUNE Tune solution under dry plasma conditions using the Aridus™ desolvating nebulizer (CETAC Technologies) for enhanced sensitivity.
3. In a third approach, the NEPTUNE Tune solution was measured at 5x higher concentration (1 ppm Sr, Nd and Hf) using the Stable Introduction System. This 5-fold increase in sample concentration roughly compensates the sensitivity enhancement going from wet plasma conditions to dry plasma conditions.

Experimental Setup for Wet and Dry Plasma

Instrumental setup

The NEPTUNE was tuned for highest sensitivity and best peak shape. Before the performance runs were started, the instrument was allowed to warm up for about 1 hour. Plasma and Aridus parameters were as follows:

Plasma Parameters	
Cool gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	0.8 L min^{-1}
Sample gas flow rate	1.0 L min^{-1}
Plasma power	1200 W
Aridus Parameters	
Sweep gas flow (Ar)	8 L min^{-1}
Nitrogen gas flow	12-16 mL min^{-1}
Spray chamber temperature	110°C
Membrane temperature	160°C

Table 1: Plasma and Aridus parameters.

The instrument was equipped with standard nickel high performance cones (HP-cones). Table 2 gives an overview of the total sample consumption for each experiment.

	Experiment 1 SIS	Experiment 2 Aridus	Experiment 3 SIS	
Concentration Sr, Nd, Hf	200	200	1000	ppb
Sample uptake	70	90	70	µl min^{-1}
Total measurement time	5	5	5	h
Total sample uptake	21	27	21	ml
Total sample consumption	4.2	5.4	21	µg

Table 2: Total sample consumption for the three experiments.

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Multicollector Configurations

Pre-aligned cup configuration files of the variable multicollector were loaded and set.

^{142}Nd	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{147}Sm	^{148}Nd	^{149}Sm	^{150}Nd
↓	↓	↓	↓	↓	↓	↓	↓	↓
L4	L3	L2	L1	C	H1	H2	H3	H4

	^{173}Yb	^{174}Hf	^{175}Lu	^{176}Hf	^{177}Hf	^{178}Hf	^{179}Hf	
	↓	↓	↓	↓	↓	↓	↓	
L4	L3	L2	L1	C	H1	H2	H3	H4

^{82}Kr	^{83}Kr	^{84}Sr	^{85}Rb	^{86}Sr	^{87}Sr	^{88}Sr		
↓	↓	↓	↓	↓	↓	↓		
L4	L3	L2	L1	C	H1	H2	H3	H4

Method and Data Evaluation

An extended electronic baseline of 300 s in defocused ion beam mode and a peak center were performed at the beginning of each run. A cross calibration (gain calibration) for 1 x $10^{11}\Omega$ and $1x10^{12}\Omega$ amplifiers was carried out once a day. The isobaric interferences were corrected by measuring the intensities of ^{83}Kr, ^{85}Rb, ^{147}Sm, ^{173}Yb and ^{175}Lu (< 0.5 mV throughout this study) with low noise $1x10^{12}\Omega$ amplifiers. The main isotopes were measured on standard $1x10^{11}\Omega$ amplifiers. The measurement time for each run was approximately 30 min. A set of 10 runs completed the whole sequence. The average of ten subsequent runs of 100 cycles of 16 s per experiment provided the basis for the calculation of the external reproducibility. A 2σ outlier test was performed at each run. Mass bias correction was done using the exponential law. We used the following normalizing ratios:

^{88}Sr/^{86}Sr = 8.375209

^{146}Nd/^{144}Nd = 0.7219

^{179}Hf/^{177}Hf = 0.7325

Results

Strontium

1. Wet Plasma Runs at 200 ppb Sr

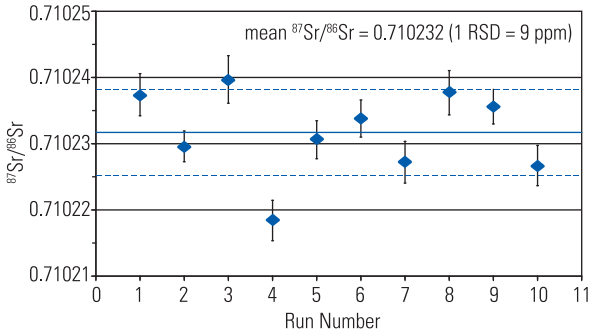

Figure 1a: Reproducibility of 10 Sr runs (wet plasma, 200 ppb).

2. Dry Plasma Runs at 200 ppb Sr

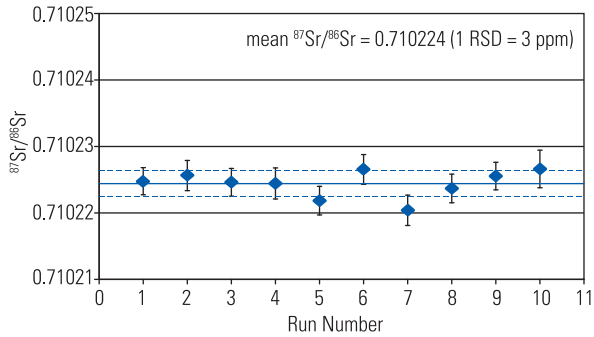

Figure 1b: Reproducibility of 10 Sr runs (dry plasma, 200 ppb).

3. Wet Plasma Runs at 1 ppm Sr

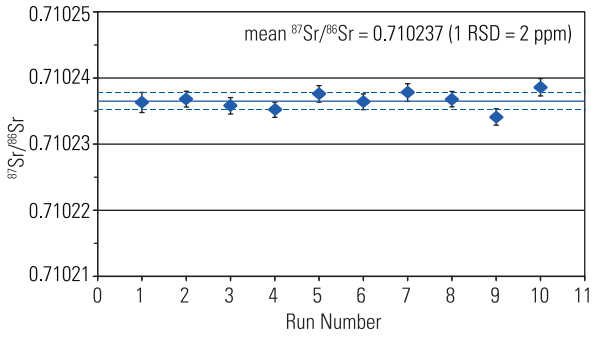

Figure 1c: Reproducibility of 10 Sr runs (wet plasma, 1 ppm).

Neodymium

1. Wet Plasma Runs at 200 ppb Nd

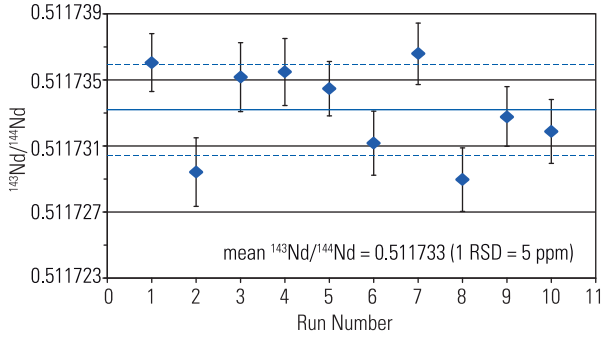

Figure 2a: Reproducibility of 10 Nd runs (wet plasma, 200ppb).

2. Dry Plasma Runs at 200 ppb Nd

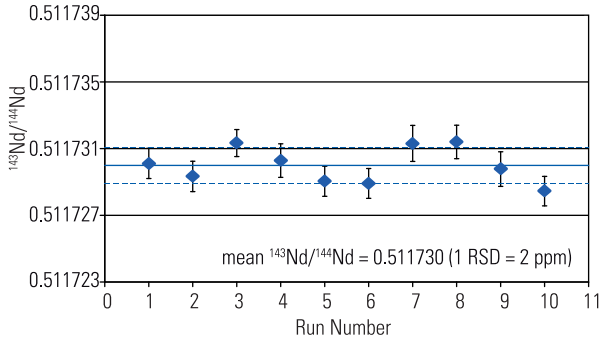

Figure 2b: Reproducibility of 10 Nd runs (dry plasma, 200 ppb).

3. Wet Plasma Runs at 1 ppm Nd

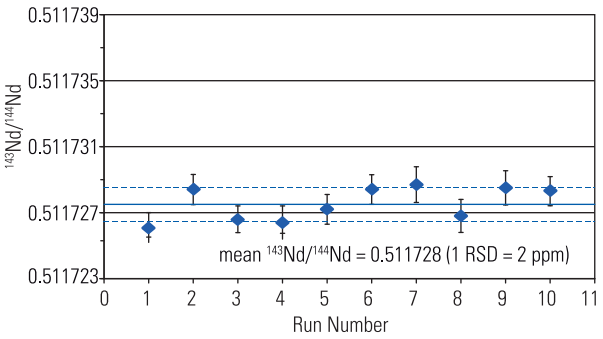

Figure 2c: Reproducibility of 10 Nd runs (wet plasma, 1 ppm).

Hafnium

1. Wet Plasma Runs at 200 ppb Hf

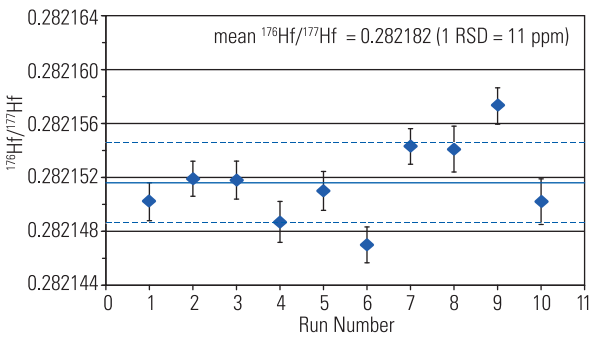

Figure 3a: Reproducibility of 10 Hf runs (wet plasma, 200 ppb).

2. Dry Plasma Runs at 200 ppb Hf

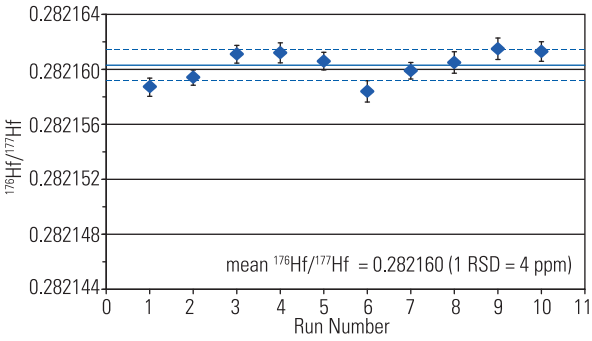

Figure 3b: Reproducibility of 10 Hf runs (dry plasma, 200 ppb).

3. Wet Plasma Runs at 1 ppm Hf

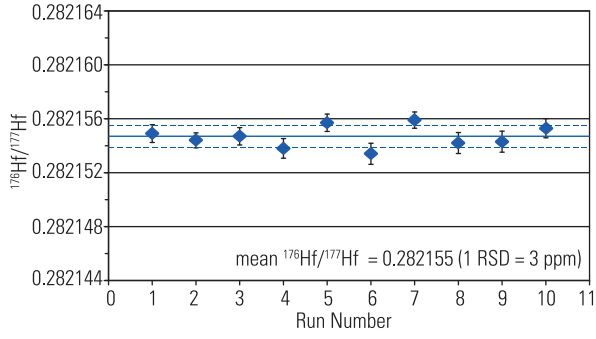

Figure 3c: Reproducibility of 10 Hf runs (wet plasma, 1 ppm).

Summary

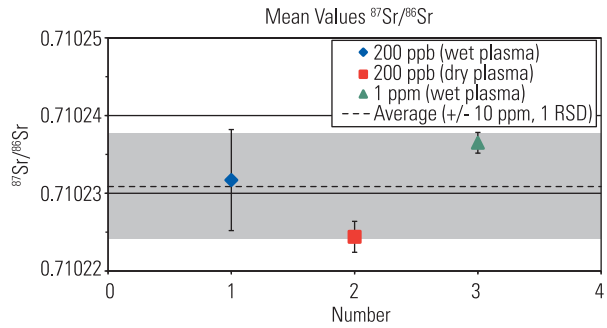

Figure 4: Mean values for Strontium. *Errors are stated in 2σ RSD (ppm).* Grey area represent 20 ppm (2 RSD) from average.

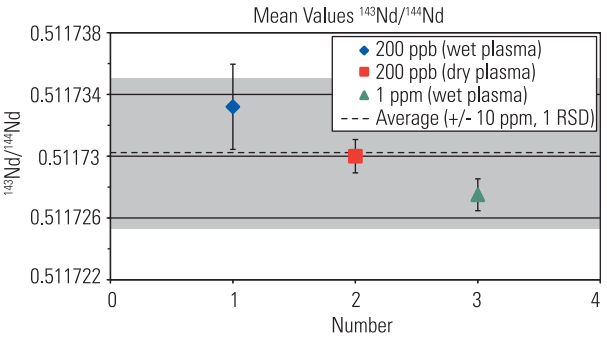

Figure 5: Mean values for Neodymium. *Errors are stated in 2σ RSD (ppm).* Grey area represent 20 ppm (2 RSD) from average.

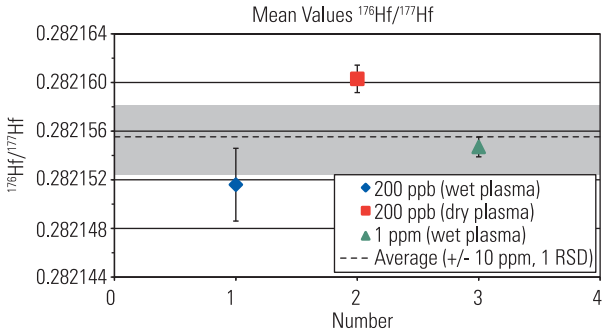

Figure 6: Mean values for Hafnium. *Errors are stated in 2σ RSD (ppm).* Grey area represent 20 ppm (2 RSD) from average.

Conclusion

Precisions for Sr, Nd and Hf isotopes ratios improve when signal intensities are increased. This is expected, as the signal-to-noise ratio is significantly improved when running at higher intensities. Precisions of 10 ppm (1 RSD) for $^{87}Sr/^{87}Sr$, $^{143}Nd/^{144}Nd$ and $^{176}Hf/^{177}Hf$ can be achieved for measurements of 1ppm using wet plasma, and 200 ppb using dry plasma. Absolute ratios for wet and dry plasma may differ due to shifting mass bias effects in the plasma source.

Appendix

Strontium

1. Wet Plasma Runs at 200 ppb Sr

Run No.	^{88}Sr (V)	$^{88}Sr/^{86}Sr$ normalizing ratio	$^{87}Sr/^{86}Sr$ normalized	Std. Error (1σ)
1	7.475	8.73797	0.710237	3.18E-06
2	7.407	8.73934	0.710230	2.32E-06
3	7.389	8.73938	0.710240	3.59E-06
4	7.354	8.73991	0.710218	3.05E-06
5	7.341	8.74037	0.710231	2.87E-06
6	7.326	8.74063	0.710234	2.80E-06
7	7.356	8.73987	0.710227	3.15E-06
8	7.369	8.74008	0.710238	3.34E-06
9	7.364	8.73989	0.710236	2.62E-06
10	7.385	8.73987	0.710227	3.04E-06
Mean	7.377	8.73973	0.710232	
SD	4.19E-02	7.32E-04	6.50E-06	
RSD (ppm)		83.8	9.1	

Table 3a: Reproducibility of 10 Sr runs (wet plasma, 200 ppb).

2. Dry Plasma Runs at 200 ppb Sr

Run No.	^{88}Sr (V)	$^{88}Sr/^{86}Sr$ normalizing ratio	$^{87}Sr/^{86}Sr$ normalized	Std. Error (1σ)
1	28.73	8.71233	0.710225	2.03E-06
2	27.77	8.71300	0.710226	2.27E-06
3	26.50	8.71336	0.710225	2.09E-06
4	25.63	8.71420	0.710224	2.34E-06
5	24.62	8.71434	0.710222	2.15E-06
6	23.57	8.71425	0.710227	2.24E-06
7	23.34	8.71471	0.710220	2.29E-06
8	22.69	8.71465	0.710224	2.15E-06
9	22.15	8.71522	0.710226	2.07E-06
10	21.24	8.71593	0.710227	2.82E-06
Mean	24.62	8.71420	0.710224	
SD	2.48E+00	1.06E-03	1.99E-06	
RSD (ppm)		121.9	2.8	

Table 3b: Reproducibility of 10 Sr runs (dry plasma, 200 ppb).

3. Wet Plasma Runs at 1 ppm Sr

Run No.	^{88}Sr (V)	$^{88}Sr/^{86}Sr$ normalizing ratio	$^{87}Sr/^{86}Sr$ normalized	Std. Error (1σ)
1	35.78	8.73567	0.710236	1.52E-06
2	35.73	8.73611	0.710237	1.19E-06
3	35.66	8.73643	0.710236	1.24E-06
4	35.58	8.73691	0.710235	1.15E-06
5	35.35	8.73741	0.710238	1.25E-06
6	35.21	8.73770	0.710236	1.19E-06
7	35.19	8.73804	0.710238	1.34E-06
8	35.20	8.73781	0.710237	1.16E-06
9	35.07	8.73811	0.710234	1.24E-06
10	34.95	8.73828	0.710239	1.31E-06
Mean	35.37	8.73725	0.710237	
SD	2.98E-01	9.16E-04	1.33E-06	
RSD (ppm)		104.9	1.9	

Table 3c: Reproducibility of 10 Sr runs (wet plasma, 1 ppm).

Neodymium

1. Wet Plasma Runs at 200 ppb Nd

Run No.	^{142}Nd (V)	^{146}Nd/^{144}Nd normalizing ratio	^{143}Nd/^{144}Nd normalized	Std. Error (1σ)
1	2.824	0.741454	0.511736	1.75E-06
2	2.802	0.741568	0.511729	2.08E-06
3	2.778	0.741665	0.511735	2.09E-06
4	2.767	0.741737	0.511736	2.03E-06
5	2.745	0.741796	0.511735	1.65E-06
6	2.746	0.741794	0.511731	1.94E-06
7	2.722	0.741876	0.511737	1.86E-06
8	2.734	0.741858	0.511729	1.92E-06
9	2.716	0.741930	0.511733	1.81E-06
10	2.683	0.741997	0.511732	1.94E-06
Mean	2.752	0.741767	0.511733	
SD	4.21E-02	1.67E-04	2.76E-06	
RSD (ppm)		224.8	5.4	

Table 4a: Reproducibility of 10 Nd runs (wet plasma, 200 ppb).

2. Dry Plasma Runs at 200 ppb Nd

Run No.	^{142}Nd (V)	^{146}Nd/^{144}Nd normalizing ratio	^{143}Nd/^{144}Nd normalized	Std. Error (1σ)
1	13.08	0.743456	0.511730	9.05E-07
2	13.24	0.743606	0.511729	9.12E-07
3	12.94	0.743692	0.511731	8.09E-07
4	12.58	0.743766	0.511730	1.01E-06
5	12.48	0.743836	0.511729	9.01E-07
6	12.18	0.743905	0.511729	8.96E-07
7	11.57	0.743967	0.511731	1.08E-06
8	11.40	0.744029	0.511731	1.00E-06
9	11.21	0.744086	0.511730	1.04E-06
10	10.95	0.744135	0.511729	8.85E-07
Mean	12.16	0.743848	0.511730	
SD	8.30E-01	2.19E-04	1.08E-06	
RSD (ppm)		294.9	2.1	

Table 4b: Reproducibility of 10 Nd runs (dry plasma, 200 ppb).

3. Wet Plasma Runs at 1 ppm Nd

Run No.	^{142}Nd (V)	^{146}Nd/^{144}Nd normalizing ratio	^{143}Nd/^{144}Nd normalized	Std. Error (1σ)
1	10.76	0.742595	0.511726	9.93E-07
2	10.51	0.742766	0.511728	8.96E-07
3	10.38	0.742837	0.511727	1.05E-06
4	10.34	0.742810	0.511726	1.05E-06
5	10.33	0.742786	0.511727	1.07E-06
6	10.27	0.742751	0.511728	9.83E-07
7	10.19	0.742762	0.511729	9.91E-07
8	10.12	0.742813	0.511727	1.03E-06
9	10.13	0.742803	0.511729	1.18E-06
10	10.10	0.742784	0.511728	8.98E-07
Mean	10.31	0.742771	0.511728	
SD	2.05E-01	6.70E-05	1.03E-06	
RSD (ppm)		90.2	2.0	

Table 4c: Reproducibility of 10 Nd runs (wet plasma, 1 ppm).

Hafnium

1. Wet Plasma Runs at 200 ppb Hf

Run No.	^{178}Hf (V)	^{179}Hf/^{177}Hf normalizing ratio	^{176}Hf/^{177}Hf normalized	Std. Error (1σ)
1	2.990	0.745180	0.282150	1.41E-06
2	2.990	0.745276	0.282152	1.30E-06
3	2.987	0.745282	0.282152	1.41E-06
4	2.989	0.745268	0.282149	1.52E-06
5	2.997	0.745281	0.282151	1.44E-06
6	3.008	0.745307	0.282147	1.33E-06
7	3.001	0.745349	0.282154	1.32E-06
8	2.991	0.745283	0.282154	1.70E-06
9	2.994	0.745229	0.282157	1.35E-06
10	2.990	0.745180	0.282150	1.69E-06
Mean	2.994	0.745264	0.282152	
SD	6.54E-03	5.35E-05	2.99E-06	
RSD (ppm)		71.7	10.6	

Table 5a: Reproducibility of 10 Hf runs (wet plasma, 200 ppb).

2. Dry Plasma Runs at 200 ppb Hf

Run No.	^{178}Hf (V)	^{179}Hf/^{177}Hf normalizing ratio	^{176}Hf/^{177}Hf normalized	Std. Error (1σ)
1	14.28	0.748952	0.282159	6.59E-07
2	14.12	0.749073	0.282159	5.52E-07
3	14.05	0.749195	0.282161	6.44E-07
4	13.93	0.749322	0.282161	7.28E-07
5	13.82	0.749434	0.282161	6.43E-07
6	13.63	0.749554	0.282158	7.80E-07
7	13.51	0.749669	0.282160	6.01E-07
8	13.25	0.749798	0.282161	7.79E-07
9	13.07	0.749926	0.282162	7.80E-07
10	12.81	0.750050	0.282161	7.11E-07
Mean	13.65	0.749497	0.282160	
SD	4.83E-01	3.68E-04	1.13E-06	
RSD (ppm)		490.4	4.0	

Table 5b: Reproducibility of 10 Hf runs (dry plasma, 200 ppb).

3. Wet Plasma Runs at 1 ppm Hf

Run No.	^{178}Hf (V)	^{179}Hf/^{177}Hf normalizing ratio	^{176}Hf/^{177}Hf normalized	Std. Error (1σ)
1	12.45	0.746443	0.282155	6.71E-07
2	12.31	0.746541	0.282154	7.38E-07
3	12.32	0.746548	0.282155	7.66E-07
4	12.25	0.746590	0.282154	6.72E-07
5	12.20	0.746640	0.282156	7.48E-07
6	12.21	0.746597	0.282153	7.59E-07
7	12.31	0.746538	0.282156	6.75E-07
8	12.32	0.746505	0.282154	7.13E-07
9	12.32	0.746502	0.282154	7.30E-07
10	12.35	0.746487	0.282155	6.76E-07
Mean	12.31	0.746539	0.282155	
SD	7.23E-02	5.83E-05	8.14E-07	
RSD (ppm)		78.1	2.9	

Table 5c: Reproducibility of 10 Hf runs (wet plasma, 1 ppm).

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