MULTIPLE-DALY DETECTORS OPTION ON THE PLASMA 3 MC-ICP-MS

A recently developed Multiple-Daly option is now available on the Plasma 3 MC-ICP-MS (Fig.1). The Daly detector offers a number of advantages over the commonly used Secondary Electron Multipliers (SEM) type ion counter: a larger dynamic range providing a good overlap with the Faraday collector, a higher gain stability, a larger peak flat for precise and accurate isotope measurement, and a longer life time. The dynamic range, gain stability and linearity of a single Daly detector fitted to a Plasma 3 MC-ICP-MS have been demonstrated in a previous study [1]. This work will present the application of a multiple-Daly system (Fig. 1) in determining isotope ratios of trace-level Nd samples.

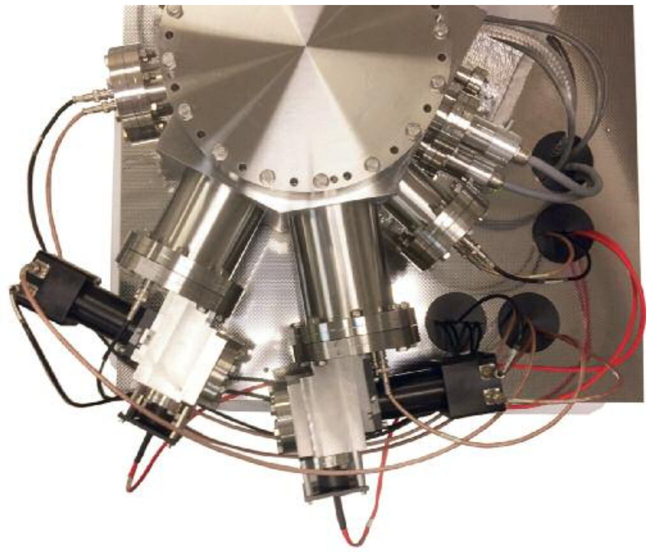

Fig 1: The multiple-Daly system.

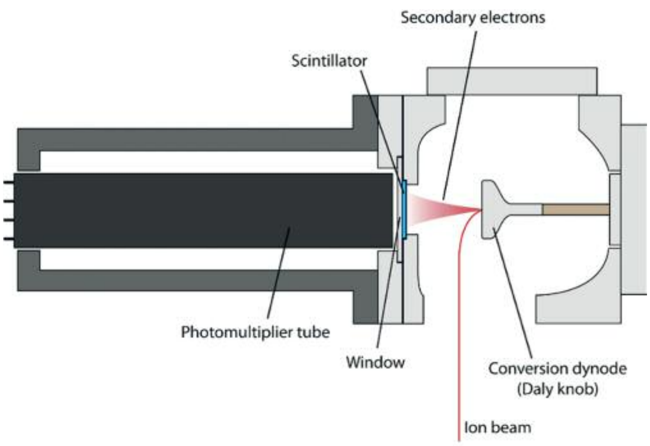

Fig 2: Principle schematic of a Daly detector.

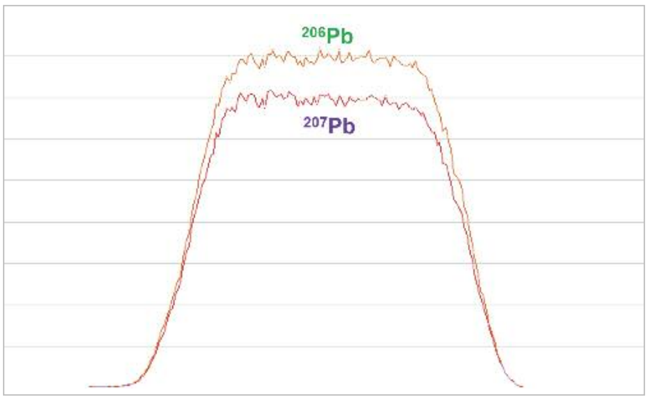

Fig 3: Typical Pb peak shapes achieved using the Plasma 3 multiple-Daly system.

Named after its inventor Norman Richard Daly, the Daly detector is a gas-phase ion counter consisting of a metal conversion dynode (Daly knob), a scintillator and a photomultiplier. Within the detector envelope, positive ions are accelerated towards the Daly knob which is held at a high negative voltage, typically between -15 kV and -25 kV. Ions strike the Daly knob to release secondary electrons, which are then repelled towards the scintillator by the high potential difference between the Daly knob and the scintillator, to form photons. These photons are then detected by the photomultiplier located outside the high vacuum (Fig. 2). This design prevents possible contamination and extends the life time of the Daly detector.

The multiple-Daly system offers a large peak flat on both detectors (Fig. 3), allowing precise and accurate simultaneous isotope determination.

In order to assess the isotope ratio determination performance of the multiple-Daly system, a Spex Certiprep (SCP) Nd standard was measured against a JNDi-1 Nd standard (Japanese Geological Survey Reference Material) using the Sample-Standard Bracketing (SSB) approach. Solution was introduced into the mass spectrometer in 2% HNO_3 under 'dry plasma' conditions, using an Aridus-II Desolvating Nebuliser system with a 100 µL/min glass concentric nebuliser and the Enhanced Sensitivity (ES) interface. Data was collected in static mode, with ^{143}Nd and ^{144}Nd measured in the two adjacent Daly detectors (Fig. 1). The other Nd isotopes were not measured. The ^{144}Sm interference on ^{144}Nd was negligible and not corrected for. Twenty repeat analyses of a 5 ppt SCP standard was bracketed by a 5 ppt JNDi-1 standard. A 2 min wash was performed after each analysis, followed by a 3 min 'on peak' zero measurement in 2% HNO_3 acid prior to the next analysis. Each analysis consisted of one block of 50 cycles of 5 sec integration. No tuning of the instrument or the Aridus-II was made once the sequence had started. The same measurement sequence was repeated for a 35 ppt SCP standard bracketed by a 35 ppt JNDi-1 standard. The sample consumption was approximately 2.1 pg for each 5 ppt analysis and 14.6 pg for each 35 ppt analysis.

In order to correct for both the mass bias and the Daly-Daly gain, the measured $^{143}Nd/^{144}Nd$ of the SCP standard was normalised to the JNDi-1 reference value of 0.5121103. The total Nd sensitivity achieved was approx. 650 volts/ppm. The ^{144}Nd beam intensity on the Daly detector was approximately 40k cps (6.4E-15 amp) and 300k cps (4.8E-14 amp) for the two concentrations, respectively. The signal remained relatively stable over the course of the sequence. The Nd oxide was consistent and well below 0.1% during the measurements. The Nd blank was less than 0.01 ppt after the 2 min wash. The total sequence duration was 431 min and 451 min, respectively.

The normalised $^{143}Nd/^{144}Nd$ of the SCP standard remained relatively consistent throughout each measurement sequence (Fig. 4), indicating a close-to-linear mass bias drift and Daly-Daly gain drift at both beam intensity levels.

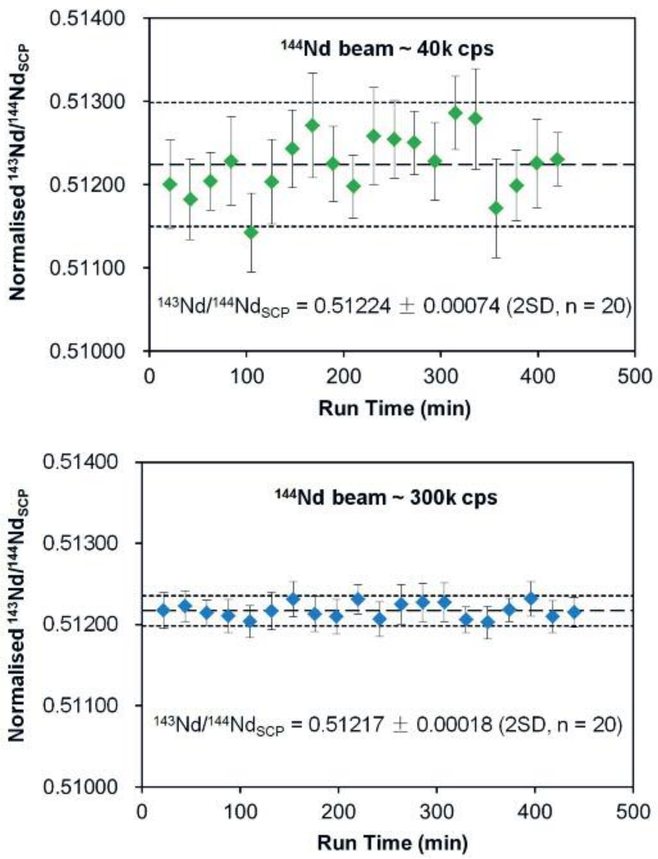

Fig 4: Normalised $^{143}Nd/^{144}Nd$ from the 5 ppt (green) and 35 ppt (blue) SCP measurements. Error bars are 2SE. The mean values are plotted in long dashed lines, ±2SD are plotted in short dashed lines..

These normalised $^{143}Nd/^{144}Nd$ measured at the two different concentrations are compared in Fig. 5. The deviation between the mean values of the two datasets is 0.01%, well within the individual measurement uncertainties. The Cosine similarity cos(θ) between the two datasets is 0.9999997, demonstrating a high level of similarity of the normalised $^{143}Nd/^{144}Nd$ measured at the two different concentrations. Therefore, the external normalisation using the JNDi-1 standard has very well corrected for the mass bias and Daly-Daly gain.

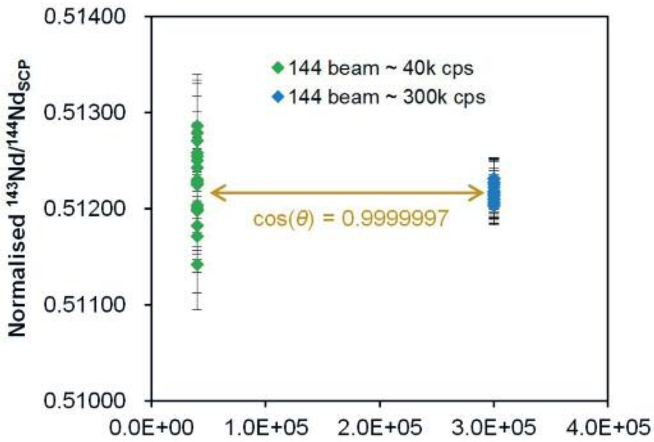

Fig 5: Comparison of the normalised $^{143}Nd/^{144}Nd$ between the 5 ppt (green) and 35 ppt (blue) SCP measurements. Error bars are 2SE. The two datasets are well within measurement uncertainties and statistically close to being identical (Cosine similarity = 0.9999997).

Table 1 compares the internal/external precisions of the normalised $^{143}Nd/^{144}Nd$ obtained in this study with the theoretical internal/external precisions based on the Johnson Noise and Shot Noise calculation [2]. It is noticed that the measurement precisions were close to or exceeded the statistical limit for the given beam intensities and measurement duration in this study. The difference between the obtained precisions and the theoretical precisions may mainly be contributed by the mass bias correction and Daly-Daly gain correction.

^{144}Nd Intensity (cps)	Analysis Duration (s)	Obtained Internal (IRSE, ppm)	Theoretical External (IRSE, ppm	Obtained External (IRSD, ppm)	Theoretical External (IRSD, ppm)
45891	250	**484**	*505*	**726**	*714*
316867	250	**190**	*192*	**184**	*271*

Table 1: Comparison between the obtained precisions (in bold) and the theoretical precisions (in italics) based on the noise calculation.

The high precisions of the trace-level Nd measurement, and the agreement with theoretical uncertainties, have demonstrated the excellent mass bias stability of the Plasma 3 MC-ICP-MS, suitability of the Sample-Standard

Bracketing approach for the mass bias correction and Daly-Daly gain correction, and the capability of the multiple-Daly system in isotope determination at such low signal levels.

Reference

[1] Gerard et al., 2015. Evaluation of high gain detection systems for the measurements of low level analytes on the Plasma 3 MC-ICP Mass Spectrometer, *European Winter Conference on Plasma Spectrochemistry 2015*.

[2] J. L. Staff, 2006. Johnson noise and shot noise, jLab E-Library, http://web.mit.edu/8.13/www/JLExperiments/JLExp43.pdf.

Appendix

Table A1: Tabulated table of the measured $^{143}Nd/^{144}Nd$ of the 5 ppt and 35 ppt JNDi-1 standard solutions. The external precision (RSD, %) of the ratio reflects the gain drift of the multiple-Daly system, in combination with the mass bias drift. The measurement sequence duration was 431 min and 451 min, respectively.

a) 5 ppt JNDi-1 solution

Analysis	$^{143}Nd/^{144}Nd$ Measured	SE	RSE (%)	^{143}Nd (cps)	^{144}Nd (cps)
1	0.52097	2.19E-04	0.042	25041	48080
2	0.52043	2.39E-04	0.046	24802	47629
3	0.52054	2.31E-04	0.044	24784	47637
4	0.52042	2.45E-04	0.047	24666	47425
5	0.52022	2.67E-04	0.051	24625	47375
6	0.52032	2.89E-04	0.056	24500	47095
7	0.51932	3.03E-04	0.058	24558	47272
8	0.52022	2.49E-04	0.048	24505	47103
9	0.51946	2.66E-04	0.051	24371	46921
10	0.51961	2.47E-04	0.048	24229	46638
11	0.51928	2.11E-04	0.041	24188	46542
12	0.51891	3.20E-04	0.062	23014	44347
13	0.51906	2.36E-04	0.045	22809	43958
14	0.51986	3.06E-04	0.059	22664	43628
15	0.51931	3.02E-04	0.058	22464	43275
16	0.51922	2.29E-04	0.044	22440	43249
17	0.52014	3.33E-04	0.064	22529	43329
18	0.51928	2.57E-04	0.049	22513	43345
19	0.51945	2.54E-04	0.049	22479	43270
20	0.51915	2.12E-04	0.041	22455	43229
21	0.51921	2.92E-04	0.056	22382	43106
Mean	0.51973				
SD	0.00059				
RSD (%)	**0.114**				

b) 35 ppt JNDi-1 solution

Analysis	$^{143}Nd/^{144}Nd$ Measured	SE	RSE (%)	^{143}Nd (cps)	^{144}Nd (cps)
1	0.52223	9.69E-05	0.019	175409	335924
2	0.52223	1.27E-04	0.024	173107	331478
3	0.52235	8.10E-05	0.016	172157	329537
4	0.52229	8.15E-05	0.016	169524	324611
5	0.52257	1.14E-04	0.022	168245	321999
6	0.52227	1.04E-04	0.020	167685	320995
7	0.52233	8.58E-05	0.016	168390	322283
8	0.52197	1.01E-04	0.019	169559	324779
9	0.52212	8.84E-05	0.017	170466	326514
10	0.52215	1.02E-04	0.020	170063	325720
11	0.52196	9.72E-05	0.019	169645	325013
12	0.52217	1.07E-04	0.020	169821	325404
13	0.52201	7.87E-05	0.015	169811	325345
14	0.52213	1.04E-04	0.020	170062	325694
15	0.52190	8.90E-05	0.017	168950	323738
16	0.52204	1.07E-04	0.020	169651	324956
17	0.52193	8.66E-05	0.017	169433	324642
18	0.52201	1.04E-04	0.020	165478	317000
19	0.52210	8.92E-05	0.017	152024	291144
20	0.52223	7.63E-05	0.015	151276	289601
21	0.52221	1.12E-04	0.021	152722	292431
Mean	0.52215				
SD	0.00017				
RSD (%)	**0.032**				