

High Precision Static Calcium Isotope Measurements

- Excellent reproducibility from general automatic operation of 1 μg Calcium 915b standard
- 23 ppm (1 RSD) Average $^{40}\text{Ca}/^{44}\text{Ca}$
- 65 ppm (1 RSD) Average $^{43}\text{Ca}/^{44}\text{Ca}$
- 26 ppm (1 RSD) Average $^{48}\text{Ca}/^{44}\text{Ca}$
- 0.28% (1 RSD) Average $^{46}\text{Ca}/^{44}\text{Ca}$

Calcium (Ca) isotopes in primitive meteorites and rocks from Earth, the Moon, and Mars can be used to provide information on early solar system processes and planetary differentiation. The isotopic measurement of Ca by thermal ionization mass spectrometry (TIMS), is often used as an indication of the performance of a TIMS instrument.

The Nu TIMS instrument with Zoom Optics allows each measurement line to be tuned for best alignment and instantly switched electronically to the next line in milliseconds during the measurement. This ensures the highest accuracy and precision without the need for movable detectors.

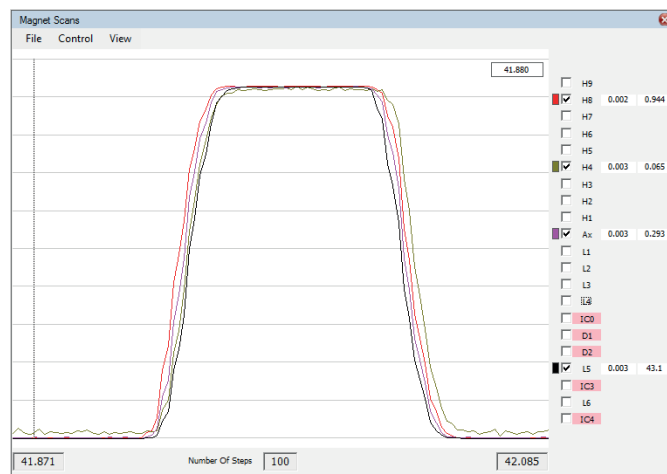


Figure 1: Peak alignment for Calcium measurement line 1

Analysis Mass Table - 2Cycle Ca.TRF																									
File	H9	H8	H7	H6	H5	H4	H3	H2	H1	Ax	L1	L2	L3	L4	IC0	D1	D2	L5	IC3	L6	IC4	Integ Time	Mass Sep	Quad 1	Quad 2
	(0)	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)				
Zero 1	47.75	47.5	47.25	47	46.75	46.5	46.25	46	45.75	45.5	45.25	45	44.75	44.5	44.25	---	---	43.5	---	---	---	160	0.25	-17	17
Meas 1	44.25	44	43.75	43.5	43.25	43	42.75	42.5	42.25	42	41.75	41.5	41.25	41	40.75	---	---	40	---	---	---	16	0.25	-17	17
Meas 2	48.25	48	47.75	47.5	47.25	47	46.75	46.5	46.25	46	45.75	45.5	45.25	45	44.75	---	---	44	---	---	---	16	0.25	4	-69.5

Maximum Sample Filament Current (if used)	3500	No. of measurements per block	10	Magnet delay time	5
Monitor Mass	40	No. of blocks	35	Centre every	1 blocks
☐ Force Time Drift Correction during run	☐ Sit on set (Delta M)	Re-Tune Source after every	1 blocks		
☐ Zero each cycle	Zoom Info from tuning file:	Calcium.Tun			

Fig 2: Detector configuration and measurement parameters for Calcium

Parameters						
Sample	Filament	Analysis Mode	Target beam intensity	Warm up	Measurement duration	Baselines
1 μg Calcium NBS 915b	Double					
	Zone refined Rhenium	Static, 35 blocks of 10 measurements	^{40}Ca 14 V	~ 1 hour	5 hours	160 seconds
						Before each block

Table of data all normalized to $^{42}\text{Ca}/^{44}\text{Ca} = 0.31221$

Ca40 (v)	2SE	1RSE (%)	40/44 corr	2SE	1RSE (ppm)	43/44 corr	2SE	1RSE (ppm)	46/44 corr	2SE	1RSE (%)	48/44 corr	2SE	1RSE (ppm)	42/44 raw	2SE	1RSE (ppm)	K41	2SE
14.07	0.14	0.50	4.7166E+01	1.52E-03	16.1	6.4869E-02	3.66E-06	28.2	1.5347E-03	3.50E-06	0.11	8.8721E-02	5.40E-06	30.4	3.0964E-01	1.11E-04	179.9	1.01E-03	1.64E-04
13.67	0.18	0.65	4.7166E+01	1.74E-03	18.5	6.4860E-02	4.10E-06	31.6	1.5425E-03	3.84E-06	0.12	8.8718E-02	5.58E-06	31.4	3.0965E-01	1.27E-04	204.7	8.29E-05	8.64E-06
13.29	0.19	0.72	4.7165E+01	1.73E-03	18.4	6.4870E-02	4.14E-06	31.9	1.5276E-03	3.98E-06	0.13	8.8715E-02	5.50E-06	31.0	3.0979E-01	6.44E-05	103.9	5.00E-04	4.00E-05
13.19	0.19	0.72	4.7165E+01	1.81E-03	19.2	6.4863E-02	4.40E-06	33.9	1.5342E-03	3.82E-06	0.12	8.8717E-02	4.98E-06	28.1	3.0978E-01	6.30E-05	101.7	2.97E-04	2.14E-05
13.90	0.21	0.76	4.7164E+01	1.66E-03	17.6	6.4873E-02	4.12E-06	31.8	1.5355E-03	3.78E-06	0.12	8.8716E-02	5.20E-06	29.3	3.0995E-01	1.39E-04	224.2	7.82E-05	8.16E-05
14.10	0.06	0.23	4.7163E+01	1.72E-03	18.2	6.4868E-02	3.86E-06	29.8	1.5362E-03	3.76E-06	0.12	8.8714E-02	5.66E-06	31.9	3.0955E-01	2.26E-04	365.0	2.27E-04	9.22E-06
Average			4.7165E+01			6.4867E-02			1.5351E-03			8.8717E-02			3.0973E-01				
StDev			0.001087544			4.25823E-06			4.36807E-06			2.27773E-06			0.000128615				
RSD (ppm)			23.1			65.6		RSD (%)	0.28			25.7			415.3				

Table1: Results for 1 µg Calcium

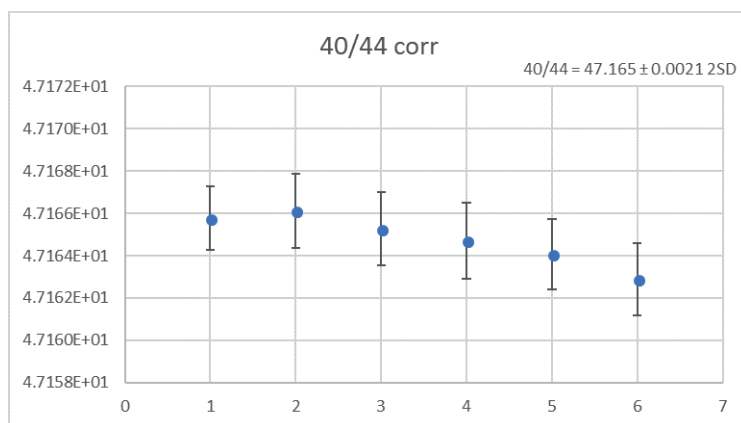


Figure 4: $^{40}\text{Ca}/^{44}\text{Ca}$ normalized to $^{42}\text{Ca}/^{44}\text{Ca} = 0.31221$, all error bars are 2 SE

Conclusion

In conclusion, 1 µg Calcium runs on Nu TIMS can give precisions below 25 ppm 1 RSD for $^{40}\text{Ca}/^{44}\text{Ca}$ using the above methods. Beam intensity is capable of increasing if improved precision is required.