

High Precision Strontium and Neodymium Isotope Analyses

Static Multiple Ion Collection and Amplifier Rotation

Dietmar Tuttas, Johannes B. Schwieters, Thermo Fisher Scientific, Bremen, Germany

Introduction

In the isotope community there has always been the vision of the perfect mass spectrometer giving accurate and precise isotope ratios without any compromise. Over the past decades major efforts were made by laboratories and manufacturers to come closer to this vision.

Thermal Ionization Mass Spectrometry (TI-MS) is a proven analytical method and is known for providing the most precise isotope ratio determinations. However, the analyst has to consider several imperfections, which contribute to the final analytical uncertainties. Some of those imperfections, which result from considerations of fundamental physical laws, cannot be overcome. But improvements and innovations in mass spectrometer hardware can still lead to improved analytical precision.

Up to the end of the 70's, single collector measurements were state of the art, resulting in analytical precisions in the range of 30 to 50 ppm at best, mostly limited by sample effects and availability of precise electronics.

Since 1980, static multiple ion collection, first shown on the Thermo Scientific MAT 261, has improved speed, precision and accuracy drastically.

Graphite-plated and extra shielded Faraday collectors of the Thermo Scientific MAT 262, together with improved electronics, pushed precisions and reproducibilities for $^{87}\text{Sr}/^{86}\text{Sr}$ or $^{143}\text{Nd}/^{144}\text{Nd}$ to 10 ppm in static multiple ion collection mode.

Special jumping procedures, so-called multi-dynamic methods, were developed to mathematically cancel out errors arising from cup imperfections and calibration uncertainties. In addition to this, cup factors were introduced to improve accuracy. However, the use of these procedures is limited to special analytical cases, e.g. if fractionation correction using internal ratios can be applied, if enough signal (data) can be collected during the sample's life, and if a present cup-error is constant during the whole run.

The analyst's vision was not fulfilled but guided to best possible answers of isotopic questions. The performance of the ion collectors (mechanics) and the measurement of the ion currents (electronics) are obviously the key areas on which to focus in the ongoing struggle to take measurements of isotopic ratios towards the limits of precision and accuracy which are imposed by ion statistics.

The Thermo Scientific TRITON has specifications for neodymium and strontium of < 5 ppm internal and external precision. Performance exceeding the specifications has been demonstrated repeatedly (Guillaume Caro, Bernard Bourdon, Jean-Louis Birck and Stephen Moorbath: *Nature*, 423, 428 - 432 (2002)).

The New Faraday Cups

The new extremely deep and wide Faraday collectors (patent issued US 6,452,165 B1) developed for the TRITON assure almost error-free data collection. They are machined from **solid graphite** to prevent or minimize escape of any reflecting secondary particles, such as secondary ions. Perfect reproducibility in manufacturing and the choice of appropriate materials assure identical behavior over a long period of time. If needed, cups can be easily and reproducibly exchanged by users, without requirement for special aligning tools. Ion beams of up to 5×10^{-10} A (50 V @ $10^{11} \Omega$) can be acquired, leading to analysis of low abundance isotopes with improved signal/noise ratio.

Amplifiers with $10^{12} \Omega$ resistors all also available, allowing further improved precision, particularly on very small isotopes (Thermo Scientific AN30136 Improvements in TI-MS High Precision Isotope Ratio Measurements for Small Sample Sizes).

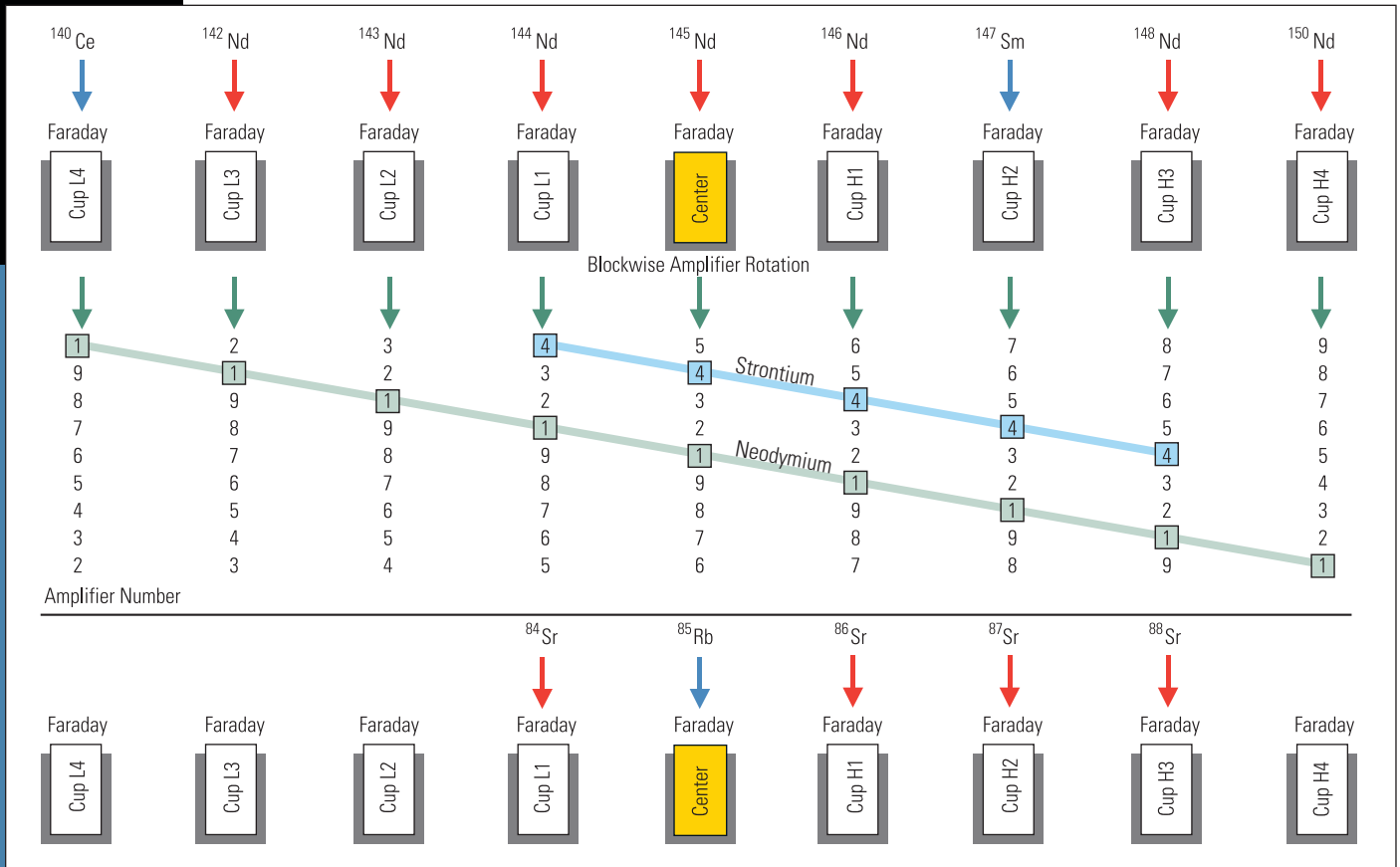
The Virtual Amplifier Concept

During the sample measurement all active cups can be cyclically connected to all amplifiers. This procedure leads to the situation that all isotopes are measured with the same set of amplifiers: the **Virtual Amplifier** (patent issued US 6,472,659 B1). This unique method combines the advantages of multi-dynamic and static measurements. In practice, all active amplifiers are sequentially switched from cup to cup. This action is performed between acquisition blocks (inter block action) within milliseconds. The number of data blocks should be at least as many or a multiple of the measured isotopes (active amplifiers). A following update of the amplifier baseline is required to assure perfect zero detection. This procedure overcomes the uncertainty barrier, imposed by the classical gain calibration of the current amplifiers.

Key Words

- TRITON
- Faraday Mode
- Nd/Sr
- Static Mode
- TI-MS
- Virtual Amplifier

Schematic of the Multi-Collector Configurations for Strontium and Neodymium

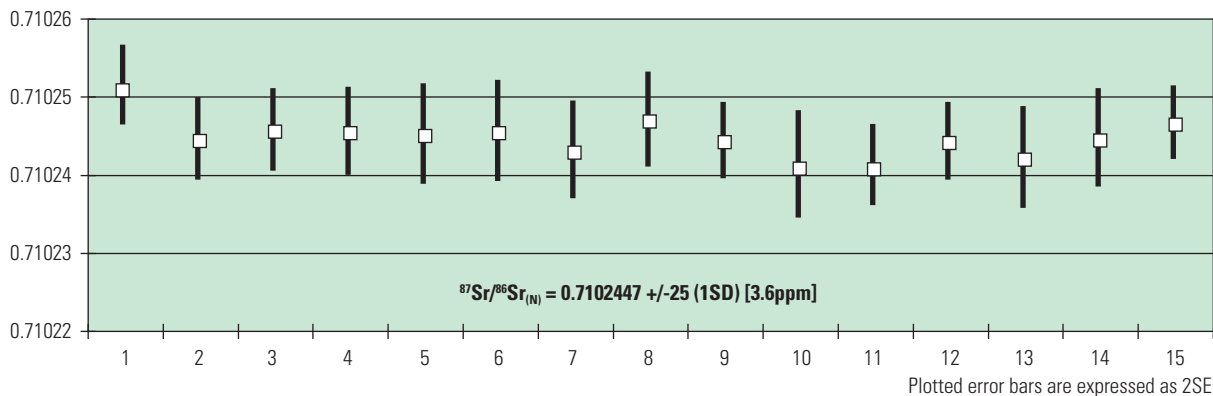


Thermo Scientific TRITON Thermal Ionization Mass Spectrometer

External Reproducibility of Fully Automatically Analyzed Strontium Standard SRM 987

RUN #	MEAN 88 INT. [V]	⁸⁶ Sr/ ⁸⁸ Sr	1SE	N NT=90	⁸⁷ Sr/ ⁸⁶ Sr (Rb-corr)	1SE	N Nt=90
1	11.42	0.0564884	0.0000011	88	0.7102512	0.0000024	88
2	11.68	0.0564896	0.0000009	86	0.7102444	0.0000025	87
3	10.18	0.0564898	0.0000010	85	0.7102455	0.0000025	88
4	10.14	0.0564927	0.0000011	87	0.7102453	0.0000027	86
5	9.74	0.0564943	0.0000012	86	0.7102450	0.0000031	86
6	9.88	0.0564924	0.0000012	87	0.7102454	0.0000031	87
7	9.63	0.0564939	0.0000012	89	0.7102430	0.0000030	89
8	11.11	0.0564905	0.0000010	87	0.7102468	0.0000029	88
9	9.72	0.0564933	0.0000010	85	0.7102442	0.0000023	86
10	9.36	0.0564927	0.0000012	89	0.7102411	0.0000033	89
11	10.59	0.0564908	0.0000011	87	0.7102410	0.0000024	85
12	9.95	0.0564917	0.0000011	86	0.7102441	0.0000023	85
13	9.87	0.0564925	0.0000012	88	0.7102420	0.0000031	87
14	12.37	0.0564939	0.0000009	89	0.7102445	0.0000030	89
15	11.02	0.0564939	0.0000011	85	0.7102464	0.0000022	84
MEAN		0.0564920	0.0000011		0.7102447	0.0000027	
SD		0.0000018			0.0000025		
RSD ppm		32.2			3.6		

Data are corrected for fractionation using ⁸⁶Sr/⁸⁸Sr=0.1194 (Exp. Law)



Analysis Parameter

Sample: 300 ng Strontium loaded onto a Re-single-filament together with Ta-activator

Sample Warm-up: Software controlled within 5 min to 2300 mA, then stepwise within 15 min to the target intensity of 12 Volt for isotope ⁸⁸Sr. Averaged filament currents are about 3000 mA.

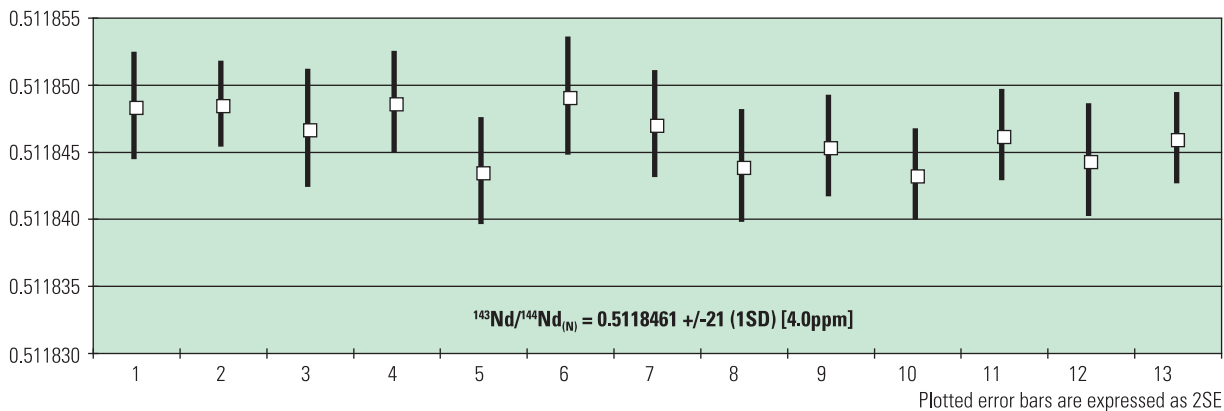
Data Acquisition: Static Faraday collection mode, amplifier rotation between data blocks

- 10 cycles, 9 blocks (90 single integrations), integration time 16 seconds per data set
- Rubidium interference is determined simultaneously and corrected using ⁸⁷Rb/⁸⁵Rb = 0.386
- Fractionation corrected using Exp. Law ⁸⁶Sr/⁸⁸Sr = 0.1194
- Outlier correction by 2-sigma-criterion

External Reproducibility of Fully Automatically Analyzed Neodymium “La Jolla”

Run #	Mean 142 Int. [V]	¹⁴² Nd/ ¹⁴⁴ Nd	1SE x 10 ⁻⁷	N Nt=180	¹⁴³ Nd/ ¹⁴⁴ Nd	1SE x 10 ⁻⁷	N Nt=180	¹⁴⁵ Nd/ ¹⁴⁴ Nd	1SE x 10 ⁻⁷	N Nt=180	¹⁴⁸ Nd/ ¹⁴⁴ Nd	1SE x 10 ⁻⁷	N Nt=180	¹⁵⁰ Nd/ ¹⁴⁴ Nd	1SE x 10 ⁻⁷	N Nt=180
1	3.46	1.1418548	50	177	0.5118483	19	176	0.3484004	11	176	0.2415774	14.0	177	0.2364568	19.0	177
2	3.47	1.1418556	40	171	0.5118484	15	171	0.3484015	13	178	0.2415805	13.0	178	0.2364576	18.0	179
3	2.94	1.1418475	53	174	0.5118466	21	179	0.3484029	14	178	0.2415790	14.0	173	0.2364592	18.0	173
4	3.29	1.1418466	47	171	0.5118486	18	171	0.3484014	12	173	0.2415815	14.0	173	0.2364562	17.0	168
5	3.51	1.1418450	53	174	0.5118434	19	170	0.3483974	12	169	0.2415801	13.0	178	0.2364591	21.0	179
6	3.27	1.1418460	57	174	0.5118490	21	176	0.3484036	14	168	0.2415798	16.0	176	0.2364600	22.0	171
7	3.97	1.1418579	50	176	0.5118469	19	176	0.3484016	11	176	0.2415845	14.0	177	0.2364598	19.0	176
8	3.21	1.1418536	64	172	0.5118438	20	172	0.3484007	13	172	0.2415846	15.0	172	0.2364619	20.0	172
9	3.86	1.1418495	55	179	0.5118453	18	179	0.3484010	13	177	0.2415797	15.0	179	0.2364525	17.0	179
10	3.64	1.1418442	47	173	0.5118432	16	167	0.3484040	12	171	0.2415794	13.0	173	0.2364542	18.0	175
11	3.58	1.1418434	49	175	0.5118461	16	175	0.3484010	11	171	0.2415802	13.0	170	0.2364568	19.0	175
12	3.07	1.1418450	50	172	0.5118443	20	172	0.3484030	11	172	0.2415826	12.0	172	0.2364511	18.0	172
13	3.65	1.1418521	42	172	0.5118459	16	171	0.3483989	11	170	0.2415801	13.0	174	0.2364503	18.0	172
MEAN		1.1418493	50.5		0.5118461	18.3		0.3484013	12.2		0.2415807	13.8		0.2364566	18.8	
SD		0.0000049			0.0000021			0.0000018			0.0000021			0.0000036		
RSD ppm		4.3	4.4		4.0	3.6		5.2	3.5		8.7	5.7		15.3	7.9	

Data are corrected for fractionation using ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 (Exp. Law)



Analysis Parameters

Sample: 300 ng Neodymium “La Jolla” loaded onto previously degassed Re-ribbons, analyses performed in double filament mode

Sample Warm-up: Software controlled, ionization filament to 4500 mA, then sample filament within 20 min to the target intensity of 4 Volt for isotope ¹⁴²Nd. Beam focus and centering performed automatically.

Data Acquisition: Static Faraday collection mode, amplifier rotation between data blocks

- 20 cycles, 9 blocks (180 single integrations), integration time 15x1 second per data set
- Fractionation correction using Exp. Law ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219
- Outlier correction by 2-sigma-criterion

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