

High Precision Strontium and Neodymium Isotope Analyses

Static Multiple Ion Collection and Amplifier Rotation

Dietmar Tutas, Johannes B. Schwieters, Thermo Electron (Bremen) GmbH, Barkhausenstrasse 2, 28197 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 Finnigan™ MAT 261, has improved speed, precision and accuracy drastically.

Graphite-plated and extra shielded Faraday collectors of the Finnigan 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 Finnigan 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 Finnigan 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} Ω) can be acquired, leading to analysis of low abundance isotopes with improved signal/noise ratio.

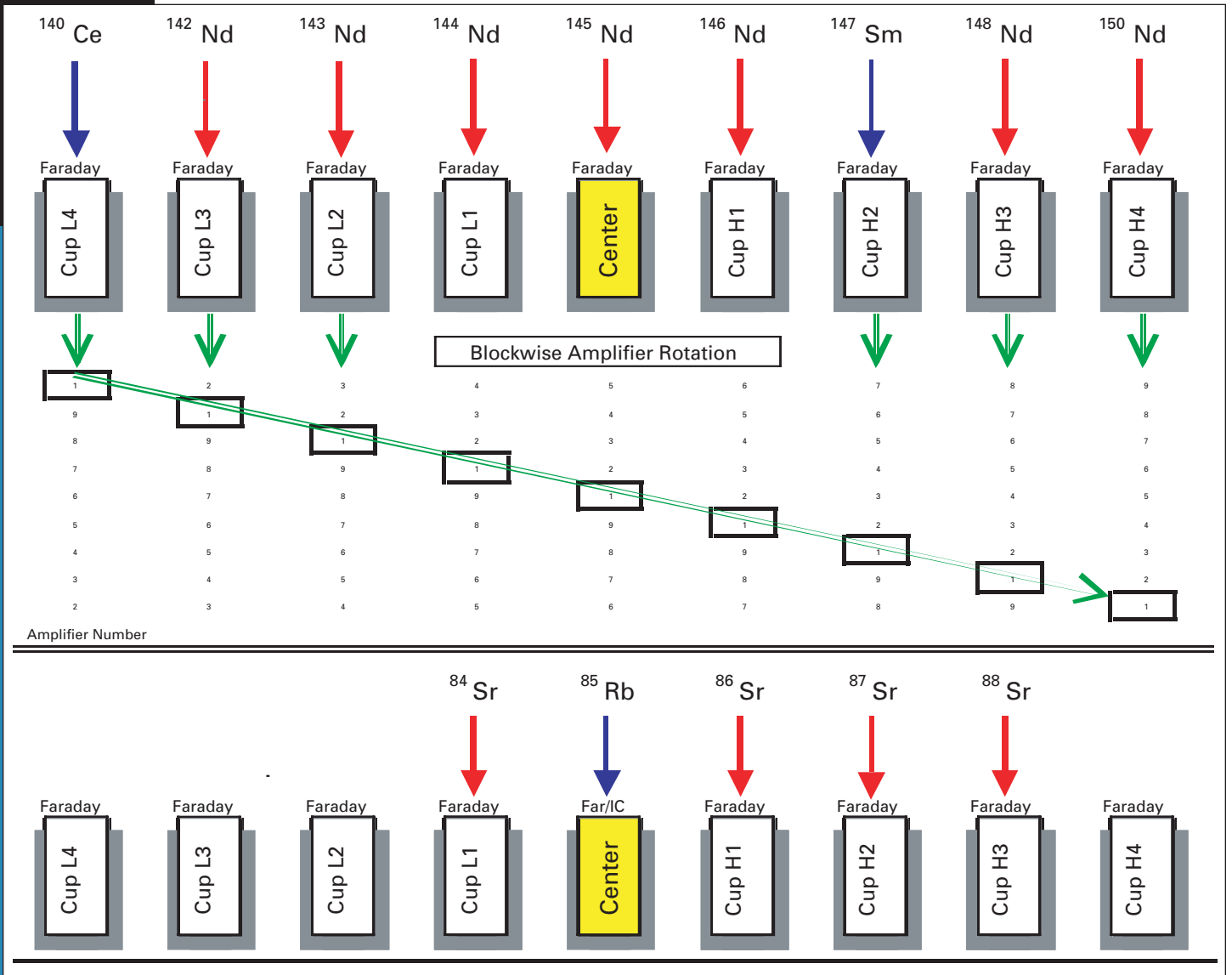
The Virtual Amplifier Concept

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 nine available amplifiers are sequentially switched from cup to cup. This action is performed between acquisition blocks (inter block action) and takes about 2s. At least nine data blocks should be acquired. This procedure overcomes the uncertainty barrier, imposed by the classical gain calibration of the current amplifiers.

Key Words

- TI-MS
- Sr
- Nd
- Static Mode
- Virtual Amplifier
- Rotation
- Faraday Mode
- Finnigan™ TRITON

Schematic of the Multi-Collector Configurations

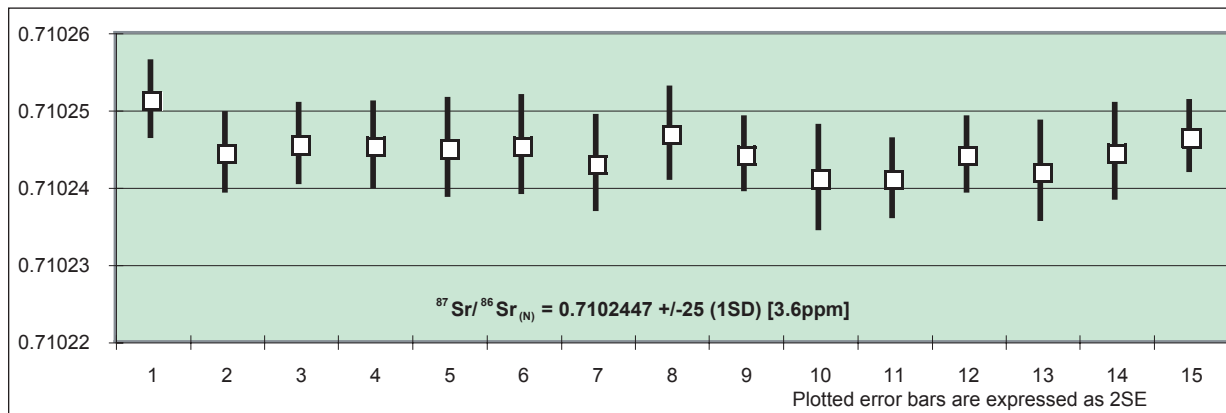


Thermal Ionization Mass Spectrometer Finnigan TRITON

External Reproducibility of fully automatically analyzed Strontium Standard SRM 987

RUN #	MEAN 88 INT. [V]	$^{88}\text{Sr}/^{86}\text{Sr}$	1SE	N NT=90	$^{87}\text{Sr}/^{86}\text{Sr}$ (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 $^{86}\text{Sr}/^{88}\text{Sr}=0.1194$ (Exp. Law)



Analysis Parameter

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

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

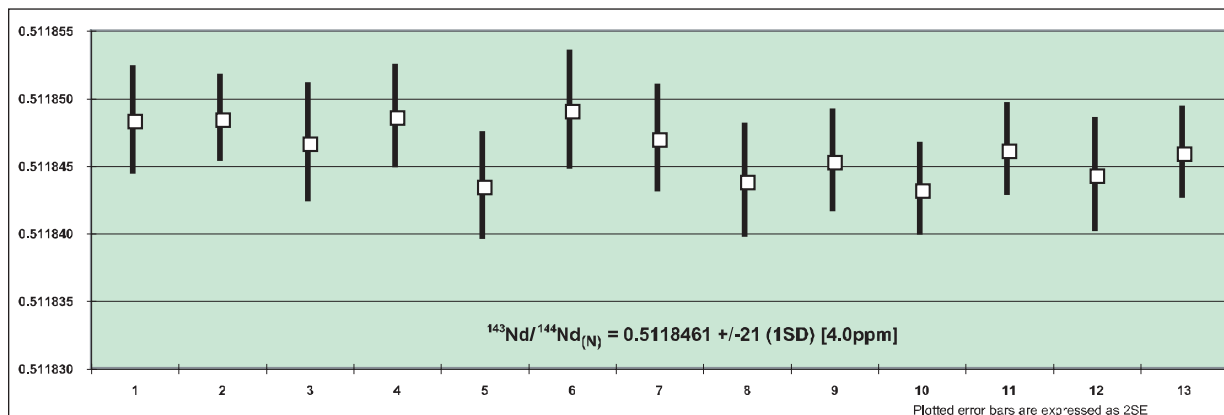
Data Acquisition: Static Faraday ion collection mode, amplifier rotation between data blocks

- 10 cycles, 9 blocks (90 single integrations), integration time 16 seconds per data set
- Rubidium interference is determined simultaneously and corrected using $^{87}\text{Rb}/^{85}\text{Rb}=0.386$
- Fractionation corrected using Exp. Law $^{86}\text{Sr}/^{88}\text{Sr}=0.1194$
- 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 N X 10 ⁻⁷ NT=180	¹⁴³ Nd/ ¹⁴⁴ Nd	1SE N X 10 ⁻⁷ NT=180	¹⁴⁵ Nd/ ¹⁴⁴ Nd	1SE N X 10 ⁻⁷ NT=180	¹⁴⁶ Nd/ ¹⁴⁴ Nd	1SE N X 10 ⁻⁷ NT=180	¹⁵⁰ Nd/ ¹⁴⁴ Nd	1SE N X 10 ⁻⁷ 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 $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ (Exp. Law)



Analysis Parameters

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

Sample Warm-up: Software controlled, ionization filament to 4500mA, then sample filament within 20 min to the target intensity of 4 Volt for isotope ^{142}Nd . 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
 $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$

- Outlier correction by 2-sigma-criterion

In addition to these offices, Thermo Electron Corporation maintains a network of representative organizations throughout the world.

Australia
+61 2 9898 1244

Austria
+43 1 333 50340

Belgium
+32 2 482 30 30

Canada
+1 800 532 4752

China
+86 10 5850 3588

France
+33 1 60 92 48 00

Germany
+49 6103 4080

Italy
+39 02 950 591

Japan
+81 45 453 9100

Netherlands
+31 76 587 98 88

Nordic
+46 8 556 468 00

South Africa
+27 11 570 1840

Spain
+34 91 657 4930

Switzerland
+41 61 48784 00

UK
+44 1442 233555

USA
+1 800 532 4752

www.thermo.com



Thermo Electron (Bremen) GmbH is certified DIN EN ISO 9001:2000

©2003 Thermo Electron Corporation. All rights reserved. All trademarks are the property of Thermo Electron Corporation and its subsidiaries.

Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details.

AN30015_E 12/03C

Thermo
ELECTRON CORPORATION