

ICP - Mass Spectrometry

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Analysis of Rare Earth Elements by Laser Ablation-ICP-MS with the NexION 2000 ICP-MS

Introduction

Over the last 30 years, the complexity of modern technology has been rapidly increasing with the demand for more

efficient and sophisticated electronic devices, from everyday consumer products like smartphones, cameras, computers, and LED lights to breakthroughs in renewable energy and battery storage as well as improvements in medical and material science. This ever-growing demand for complex technologies is primarily due to the use and applications of the unique properties that rare earth elements (REEs) can provide, including magnetic, catalytic, and phosphorescent properties.

Rare earth elements (REEs) are seventeen chemical elements in the periodic table, including the lanthanides, yttrium, and scandium. These elements can be found in nature, but because of the reactivity of REEs, they are not naturally found in a pure metal form. Instead, they occur together in various ores and minerals that require additional extraction and separation processes. Once REEs have been isolated, they can be utilized for a wide range of applications from manufacturing processes (ceramics, autocatalytic converters, and industrial catalysts) to improvements in reduced energy consumption, greater efficiency, and miniaturization, durability, and thermal stability for electronic devices.

With the increasing development of high-tech applications, REEs are considered vital elements for modern and future industries. Globally, there is growing pressure for analytical solutions that can accurately characterize and quantify REE content in a high-throughput manner to meet the application needs of expanding industries with reliable results to a diverse selection of mineral samples.

This application note describes the *in situ* analysis of certified reference materials (CRMs) in selecting five mineral matrices using PerkinElmer's NexION® 2000 ICP-MS coupled to a laser ablation system to demonstrate the performance capabilities of laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) for quantifying rare earth elements. The content covers instrument setup, sample preparation, calibration, and analytical approach to determining the accuracy, precision, percent recovery, calculated uncertainty, and detection limits for the selection of samples and matrices used in this experiment.

Experimental

Samples and Preparation

In this application work, certified reference materials (CRMs) were purchased with various elemental concentrations and prepared for five different sample matrices, including diorite, sediment, andesite, obsidian, and basalt.

Certified reference materials (CRMs) were prepared using a lithium metaborate fusion procedure by mixing 0.6 g of CRMs with 6 g of fusion flux with the content percentages listed in Table 1.

Table 1. Composition of Fusion Flux.

Material	Content
Lithium Tetraborate, Li ₂ B ₄ O ₇	49.75%
Lithium Metaborate, LiBO ₂	49.75%
Lithium Bromide, LiBr	0.5%

Fusion beads prepared from five different matrices of CRMs labeled in Table 2 were used for calibration.

Table 2. Elemental Concentration (mg kg⁻¹) in CRMs.

	STD 1	STD 2	STD 3	STD 4	STD 5
Matrix	Diorite	Sediment	Andesite	Obsidian	Basalt
CRM ID	SY4	STSD-3	JA-1	133	134
Sc	1.1	13	28.5	38.1	5.1
Y	119	36	30.6		
La	58	39	5.24		
Ce	122	63	13.3	13.3	62.2
Pr	15		1.71		
Nd	57	33	10.9		
Sm	12.7	7	3.52	2.79	5.7
Eu	2	1.3	1.2	1.07	0.84
Gd	14		4.36		5.3
Tb	2.6	1.1	0.75	0.448	1.00
Dy	18.2	5.4	4.55		
Ho	4.3		0.95		
Er	14.2		3.04		
Tm	2.3		0.47		
Yb	14.8	3.4	3.03	2.09	4.50
Lu	2.1	0.8	0.47	0.34	0.73
Th	1.4	8.5	0.82		12.4
U	0.8	10.5	0.34	0.37	4.58

Note: Some CRMs do not contain concentration information for certain elements, hence, they were left blank in the table.

Instrumentation

All analyses were performed using an LSX-213 G2+ laser ablation system equipped with a HelEx II ablation cell (Teledyne Cetac Technologies, Omaha, Nebraska, USA) coupled to a NexION 2000 quadrupole ICP-MS system (PerkinElmer Inc., Shelton, Connecticut, USA) using the parameters in Tables 3 and 4.

Laser sampling was done in a straight line from one point to another at a defined scan rate of 10 μm/s, with a spot size of 50 μm, enough to complete measurement of 18 elements in less than one minute (58 seconds).

A HelEx II cell was used in this application. Having two separate cell flow controls (inner and outer) allows the signal intensity and washout to be optimized to the NexION 2000 ICP-MS, the ideal solution for high-throughput laboratories conducting low-level analyses in rare earth elements.

Table 3. Instrument Parameters.

Laser Ablation System	
Instrument	Teledyne Cetac LSX-213 G2+ with HelEx II Ablation Cell
Laser Fluence	6.69 J/cm ²
Laser Rep Rate	20 Hz
Spot Size	50 μm
Scan Speed	10 μm/s
Scan Time	58 s
He Gas Flow	0.65 and 0.35 L/min
ICP-MS System	
Instrument	PerkinElmer NexION 2000 ICP-MS
RF Power	1500 W
Nebulizer Gas Flow	1.04 L/min
Auxiliary Gas Flow	1.2 L/min
Plasma Flow	15 L/min
Measurement Mode	20 Replicates
Monitored Isotopes	18

Table 4. Analytes, Their Masses, and Used Dwell Time.

Element	Mass (amu)	Dwell Time (ms)	Element	Mass (amu)	Dwell Time (ms)
Sc	45.0	20	Tb	158.9	20
Y	88.9	20	Dy	162.9	20
La	138.9	20	Ho	164.9	10
Ce	139.9	20	Er	165.9	20
Pr	140.9	10	Tm	168.9	10
Nd	145.9	10	Yb	172.9	20
Sm	146.9	10	Lu	174.9	10
Eu	152.9	10	Th	232.0	20
Gd	156.9	20	U	238.1	20

Results and Discussion

Calibration

Five different matrices with various concentrations were used to construct a calibration curve (Table 5). Good correlation coefficients of calibration curves shown in Table 6 indicate that analyte responses are similar regardless of the matrix. It also demonstrates that samples prepared as fusion beads with different matrix compositions can be analyzed against calibration curves obtained that way.

Table 5. Calibration Standards Used for Five Calibration Points.

	STD 1	STD 2	STD 3	STD 4	STD 5
Matrix	Diorite	Sediment	Andesite	Obsidian	Basalt
CRM ID	SY4	STSD-3	JA-1	133	134

Table 6. Summary of Calibration Curve Results.

Analyte	Mass (amu)	Curve Type	Slope	Intercept	Corr. Coeff.
Sc	45.0	Simple Linear	110.61	149.47	0.996927
Y	88.9	Simple Linear	91.08	-118.81	0.999999
La	138.9	Simple Linear	206.24	-175.75	0.995163
Ce	139.9	Simple Linear	203.12	-70.72	0.999612
Pr	140.9	Simple Linear	213.31	115.75	1.000000
Nd	145.9	Simple Linear	33.50	21.80	0.999814
Sm	146.9	Simple Linear	30.22	-7.78	0.997846
Eu	152.9	Simple Linear	110.95	-8.11	0.995199
Gd	156.9	Simple Linear	28.66	-13.44	1.000000
Tb	158.9	Simple Linear	179.48	-2.67	0.996987
Dy	162.9	Simple Linear	44.49	20.44	0.999890
Ho	164.9	Simple Linear	170.75	39.79	1.000000
Er	165.9	Simple Linear	59.88	6.96	1.000000
Tm	168.9	Simple Linear	185.25	-6.57	1.000000
Yb	172.9	Simple Linear	31.99	-7.13	0.998124
Lu	174.9	Simple Linear	179.88	4.68	0.999912
Th	232.0	Simple Linear	227.36	-22.37	0.998836
U	238.1	Simple Linear	253.84	56.48	0.997054

Note: Calibration curve obtained with different mineral matrices.

CRM Recovery and Establishing Measurement Uncertainty

Measurement uncertainty is calculated based on the EURACHEM/CITAC Guide* - Quantifying Uncertainty in Analytical Measurement. To obtain the uncertainty, a CRM SY4 was analyzed over a period of 10 days. From these measurements, the recoveries were obtained and the uncertainty calculated (Table 7).

Most elements in CRM SY4 showed good recoveries, which fall within 90-110%, except for Lu, Th, and U that were within 90-120% due to their concentration at the low side of 0.8-2.1 mg/kg.

Uncertainties for all elements obtained here were based on a coverage factor of two with a confidence level of 95% and a relatively low range of possible values where the true value of the measurement lies.

Table 7. QC Recovery and Uncertainty Data.

Element	% Range of QC Check	Measurement Uncertainty $\bar{X} \pm$ mg/kg
Sc	83.8-109.8	0.12
Y	98.0-106.9	0.03
La	98.0-106.3	0.03
Ce	97.7-107.4	0.03
Pr	97.9-108.3	0.03
Nd	95.1-106.6	0.03
Sm	91.9-106.7	0.05
Eu	91.2-108.3	0.04
Gd	97.5-108.0	0.04
Tb	94.3-103.5	0.05
Dy	95.2-104.0	0.04
Ho	96.9-105.9	0.03
Er	93.3-104.9	0.05
Tm	91.8-107.0	0.05
Yb	92.7-105.4	0.04
Lu	93.5-114.0	0.06
Th	93.4-111.0	0.13
U	94.0-117.0	0.15

Detection Limits

Seven separate analyses of a CRM SY4 with the lowest weight (~0.1 to 6 g fusion flux) were performed. From the standard deviation of these seven readings, the limit of detection and limit of quantitation were tabulated (Table 8).

Table 8. Limit of Detection (LOD) and Limit of Quantitation (LOQ) of Elements with LA-ICP-MS.

Element	LOD (3.14 x SD) mg/kg	LOQ (10 x SD) mg/kg
Sc	< 0.5	< 2
Y	< 2	< 10
La	< 1.5	< 5
Ce	< 3.5	< 10
Pr	< 0.5	< 2
Nd	< 2.0	< 5
Sm	< 1.0	< 5
Eu	< 0.2	< 0.5
Gd	< 1.5	< 5
Tb	< 0.2	< 0.5
Dy	< 1.0	< 5
Ho	< 0.2	< 1
Er	< 0.7	< 5
Tm	< 0.2	< 1
Yb	< 1	< 5
Lu	< 0.2	< 0.5
Th	< 0.2	< 0.5
U	< 0.2	< 0.5

Accuracy (Bias) and Precision Results

Two sets of experiments were carried out to determine accuracy and precision (Table 9):

- (A) Set of experiments prepared on the first day by the first operator on CRM SY4
- (B) Set of experiments prepared on the second day by the second operator on CRM SY4

Each experiment was set up with ten separate preparations of fusion bead (verification from sample preparation) and analyzed as samples after calibration to verify the reproducibility, repeatability and inter-laboratory precision of this method.

Table 9. Accuracy (Bias) and Precision Study on CRM SY4.

Element	Certificate	Accuracy (Bias) and Precision			
	Concentration mg/kg	(A) Bias %	(B) Bias %	(A) Precision %	(B) Precision %
Sc	1.1	13.82	-12.78	8.29	9.73
Y	119	7.10	-4.47	3.47	1.73
La	58	3.55	-8.12	2.98	1.86
Ce	122	1.18	-12.26	3.38	2.05
Pr	15	3.82	-12.78	3.29	1.73
Nd	57	3.17	-13.11	2.77	1.91
Sm	12.7	-0.85	-10.30	4.75	4.27
Eu	2	-2.40	-11.09	2.25	4.13
Gd	14	-3.54	-8.38	3.48	3.19
Tb	2.6	-0.74	-8.56	2.49	2.01
Dy	18.2	0.21	-7.78	3.53	2.00
Ho	4.3	-0.24	-10.38	2.81	1.99
Er	14.2	-1.06	-8.66	3.98	2.34
Tm	2.3	-0.60	-10.45	4.86	4.19
Yb	14.8	-2.94	-8.54	4.61	2.22
Lu	2.1	-0.09	-7.00	4.56	3.86
Th	1.4	2.86	-1.87	3.80	3.36
U	0.8	15.07	-7.58	6.30	6.24

Conclusion

The method developed here is fast and straightforward (as short as 58 seconds for 18 elements) and has excellent accuracy and precision. The XRF technique can be used to complement LA-ICP-MS – the same sample analyzed via LA-ICP-MS for REE determination can also be analyzed via XRF for main elements in minerals, including Na, Mg, Al, Si, P, K, Ca, Ti, Mn, and Fe.

The method's validity has been verified by incorporating robustness and ruggedness tests on energy output, different mineral matrices, and additional sample preparation weights in the fusion bead. The CRM recovery, QC and spike recovery checks throughout the analysis showed good recoveries, well within acceptable limits, demonstrating that the NexION 2000 ICP-MS coupled to a laser ablation system can achieve excellent detection limits with good accuracy (bias %) and precision (repeatability %) well within acceptable limits.

Consumables Used

Component	Part Number
Baffled Cyclonic Spray Chamber	N8152389
MEINHARD® Nebulizer	N8152373
One-piece Quartz Torch with 2.5 mm Injector, PVDF O-ring Freeholder (Blue Mark) Torch	N8152473