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Analysis of Samples Rich in Rare Earth Elements Prepared by Lithium Borate Fusion on the NexION 5000 ICP-MS

Introduction

When the term "rare earth elements" (REEs) is used, it typically refers to a group of elements including the lanthanide series (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) as well as Sc and Y. REEs have many uses in the advanced technology and electronics that are utilized in automobiles, airplanes, camera lenses, medical devices, televisions, smartphones, and computers, to name a few. With the growing demand for REEs to support technological advancement, the search for larger REE deposits and quality ore material is ongoing. Since raw geological materials that contain REEs are usually only found in low concentrations, an essential component of geological exploration is the ability to accurately quantify and detect REEs in the collected geological samples since this determines the viability of new mine sites and can help to expand existing ones.

Commonly used techniques to analyze REEs in geologic materials are inductively coupled plasma mass spectrometry (ICP-MS), x-ray fluorescence (XRF), and instrumental neutron activation analyses (INAA). While INAA and XRF have their respective advantages and disadvantages, they both suffer from poor detection limits compared to ICP-MS, which is necessary to detect low concentration REEs.

For this reason, the measurement of REEs by ICP-MS following sample preparation is a more widely used analytical technique. Appropriate sample preparation before analysis by ICP-MS is crucial to deliver accurate results – where this is usually a fusion or acid digestion method. Depending on the preparation method chosen, various complications to the analysis may be introduced. The preparation technique of fusing samples in lithium borate flux is widely used for matrices that are very refractory and otherwise hard to digest.

In ICP-MS analysis, the high lithium and boron backgrounds in these types of prepared samples can present some challenges in sample introduction and matrix effects due to the increased amount of total dissolved solids (TDS) in the prepared solution, and these issues need to be addressed. Moreover, since REEs are usually present in very low concentrations, and many have isotopic and oxide overlaps, these factors can provide additional considerations. The combination of the All Matrix Solution (AMS, an online argon dilution system)[1], second-generation Triple Cone Interface with OmniRing™ technology[2], four gas channels with on-line gas mixing, Universal Cell Technology (UCT), and multi-quadrupole design of PerkinElmer's NexION® 5000 ICP-MS provides many of the tools needed to overcome these issues.

This work will describe the analysis of three certified reference materials (CRMs) containing REEs that have been prepared by fluxing the samples with lithium borate. These samples are comprised of different ore materials, all containing REEs, and are analogous to exploration samples.

Experimental

Samples and Sample Preparation

In this application note, an external laboratory provided certified reference materials (CRMs) that had already undergone lithium metaborate/tetraborate fusion and subsequent dissolution in 5% HNO_3 (ca. 100 mg of sample, 100 mL dilution). An additional dilution of 100x was performed on each CRM before analysis using a diluent of 0.5 % HNO_3. The CRMs used were REE-1, REE-2, and REE-3 (CanMET Mining, Ottawa, Ontario, Canada). Blank fusion solutions were also provided so that calibration standards and blanks could be matrix matched. The standard concentrations prepared for all samples were 0.2, 2 and 20 ppb. For elements Al, Ca, Fe, K, Mg, Na, and Si, the standard concentrations were 0.2, 2, 20, 200, and 400 ppb. Due to the complex and heavy matrix, 10 ppb rhodium was used as the internal standard and added online through the internal standard port of PerkinElmer's High Throughput System (HTS), a flow injection sample introduction module.

Instrumental Conditions

All analyses were performed on a NexION 5000 ICP-MS, which comes equipped with both a SMARTintro™ Ultra High Purity quartz torch and a fixed 2.0 mm injector, a SilQ spray chamber, and a PFA nebulizer. The NexION's All Matrix Solution (AMS) was used for argon-based aerosol dilution to further reduce the matrix suppression resulting from the lithium borate fusion.

A PC3 spray chamber chiller was used to analyze these samples to aid in long-term stability. The HTS (High Throughput System) module was utilized to increase throughput through its vacuum-loaded sample loop and flow injection system. Specific instrument conditions can be found in Table 1.

Table 1. NexION 5000 ICP-MS Instrumental Conditions.

Parameter	Value
Plasma Gas Flow	16
Aux Flow	1.2
RF Power (W)	1600
Neb Gas Flow	0.99
AMS Gas Flow	0.11
Peltier Cooler Temp	10 °C
Pump Tubing - Carrier	Green/Orange
Pump Tubing - IS	Green/Orange
Sample Uptake Rate (mL/min)	0.14

Multiple cell modes were used to best utilize the interference removal capabilities of the NexION 5000 system. Optimization of collision and reaction gas flows, dynamic bandpass filtering within the quadrupole Universal Cell and m/z selection for the main resolving quadrupoles were all automated through Syngistix™ for ICP-MS software. The ion guide mode for all analytes was selected based on the mode which delivered the lowest background equivalent concentrations (BECs) for the analytes of interest. However, depending on the interferences present on the specific analyte, a combination of gas profiles was utilized as described in Table 2, providing examples of why multi-quadrupole technology, paired with multiple gas channels, offers superior analytical options compared to less advanced instrumentation.

A significant advantage of multi-quadrupole instruments is the ability to mass-shift a target element by reacting with a reactive gas to a higher mass and away from interferences, resulting in potentially erroneous results. Oxygen can be used to form oxides on the target elements, shifting 16 amu higher. In contrast, gases such as pure ammonia can create cluster ions with certain elements, shifting even further up the mass range and away from potential interferences. All these reactions need to be actively controlled to prevent run-away reactions from taking place. The customizable bandpass tuning afforded by the unique quadrupole UCT provides users the flexibility to actively prevent reaction byproducts from forming and reacting with the reaction gas or impurities in the gas.

Table 2. Elements Analyzed, Gas Modes, and Quadrupole Settings.

Analyte	Gas Mode	Isotope Q1/Q3
Al	Ammonia DRC	27/27
Ba	STD	137/137
Ca	Ammonia DRC	40/40
Ce	Ammonia DRC	140/140
Co	Ammonia DRC	59/59
Cr	Ammonia DRC	52/52
Cs	STD	133/133
Cu	Ammonia DRC	65/65
Dy	Oxygen DRC	163/179
Er	Oxygen DRC	166/182
Eu	Oxygen DRC	153/169
Fe	Ammonia DRC	56/56
Gd	Oxygen DRC	157/173
Hf	Oxygen DRC	178/194
Ho	Oxygen DRC	165/181
K	Ammonia DRC	39/39
La	Oxygen DRC	139/155
Lu	Oxygen DRC	175/191
Mg	Ammonia DRC	24/24
Mn	Ammonia DRC	55/55
Na	STD	23/23
Nb	Ammonia DRC	93/93
Nd	STD	143/143
P	Oxygen DRC	31/47
Pb	STD	208/208
Pr	Oxygen DRC	141/157
Sc	Oxygen DRC	45/61
Si	Ammonia/Hydrogen DRC	28/28
Sm	Oxygen DRC	147/163
Sn	STD	118/118
Sr	Ammonia DRC	88/88
Tb	Ammonia DRC	159/174
Th	STD	232/232
Ti	Ammonia DRC	48/114
Tm	Oxygen DRC	169/185
U	STD	238/238
Y	Oxygen DRC	89/105
Yb	Oxygen DRC	172/188
Zn	Ammonia DRC	66/66
Zr	STD	90/90

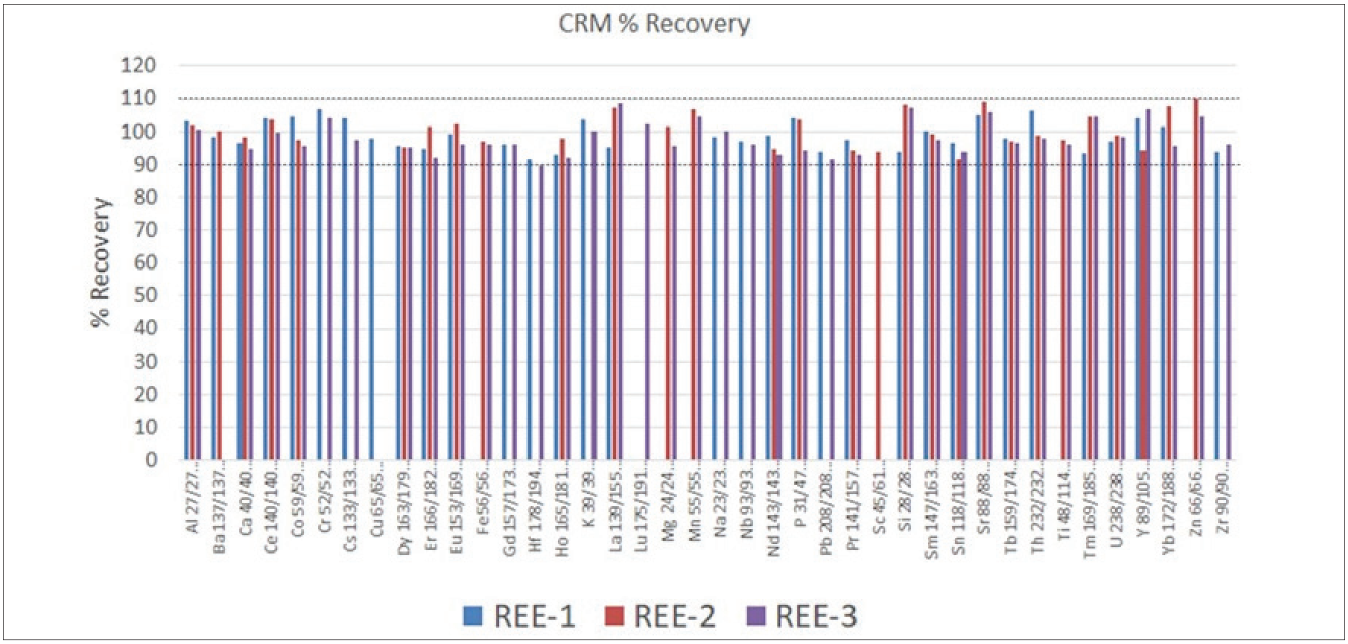

Figure 1. Analyte recoveries in certified reference materials REE-1, REE-2, and REE-3. Not all elements are certified in each reference material.

Results and Discussion

The accuracy of the methodology was established through the analysis of the three reference materials described above. Shown in Figure 1, 80% of the analyte recoveries are within 5% of the certified values and 100% within 10% of the certified values. In particular, note the conditions used for Si and P as an example of the flexibility of the Universal Cell's reaction capability. For Si, ammonia and hydrogen are mixed online in the cell for the best interference removal of N_2 and CO on mass 28. Phosphorus, on the other hand, is monoisotopic with 100% isotopic abundance at 31 amu. However, there are interferences from N and Si on this mass (NOH, SiH, NO), which can typically make the analysis challenging for single quadrupole instruments. However, with multi-quadrupole ICP-MS technology, P is mass shifted to PO and examined clear of these interferences, providing excellent CRM recoveries (Figures 1 and 2, respectively).

Figure 2 shows the results of a spike recovery test (4 ppb spike) conducted on REE-1 as an additional test of accuracy where all elements were recovered within 10% of the expected results. Since the heavier REE elements are typically plagued by interferences from the lower mass REE elements' oxides, most of these elements were measured using Mass Shift mode with oxygen as a reaction gas in the cell. This was done to take advantage of these elements' propensity to produce oxides quickly in a kinetically favorable reaction that mass shifts them away from interferences (Table 2). The spike recoveries for the REE elements are close to 100%, demonstrating that the interferences have been efficiently removed. Had this not been the case, higher than expected recoveries for higher-mass REE elements from Sm to Lu would have been observed.

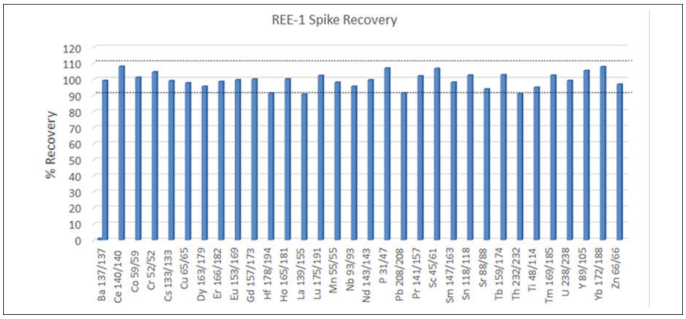

Figure 2. A 4 ppb spike was performed on the CRM REE-1. This spike level was too low for a proper spike recovery test on Al, Ca, Fe, K, Mg, Na, Si, and Zr in this CRM.

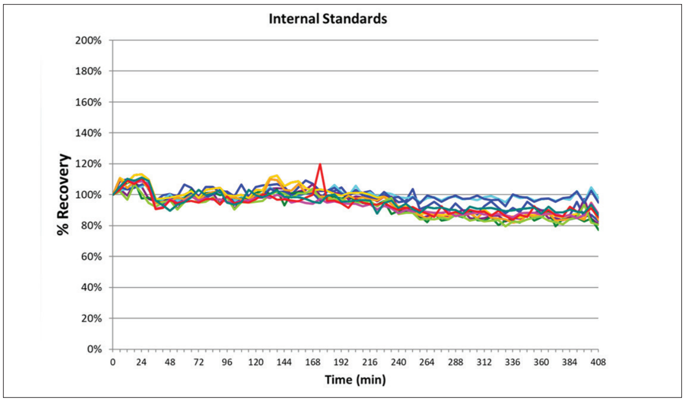

Figure 3. Long-term stability based on internal standard (Rh) measured over a nearly 7-hour run with multiple gas modes.

Long-term stability was verified during a seven-hour analysis of the lithium borate fused samples. The analytical run consisted of multiple fusions of each CRM, repeated in sequence, as well as matrix blanks and simulated samples in the same fusion matrix, all to demonstrate the effect of analyzing samples with high total dissolved solids (TDS) on the sample introduction and internal components of the NexION 5000 ICP-MS. The internal standard recoveries relative to the calibration blank were monitored and are shown in Figure 3. All internal standards recovered within 20% of their values being standardized to their response within the calibration blank, further validating the method's robustness and analytical instrumentation. This outstanding performance is the direct result of NexION 5000's instrumental design considerations, such as its solid-state, free-running RF generator[3], Triple Cone Interface[2], and Quadrupole Ion Deflector. The use of AMS also aids in maintaining long-term stability through an argon dilution effect which reduces matrix build-up on the cone system.

Conclusion

The analyses described within this application note demonstrate the accurate and highly stable quantification of REEs and other elements of interest in geological samples. The NexION 5000 Multi-Quadrupole ICP-MS was determined to deliver outstanding robustness, even for sample types that would typically present analytical challenges, thanks to AMS and the combination of the Triple Cone Interface with OmniRing technology. Moreover, superior interference removal was achieved on all analytes of interest. In many cases, Multi Quad mode was able to ensure control of the ions that enter the cell and the reactions within the cell. Furthermore, having four gas channels enabled maximum specificity in the reaction chemistry such that the most effective single or mixed reaction gas could be used without compromise.

References

1. All Matrix Solution System for NexION ICP-MS Platforms, PerkinElmer Technical Note, 2017.
2. Advantages of a Novel Interface Design for NexION 5000 ICP-MS, PerkinElmer Technical Note, 2020.
3. Advantages of a Novel Plasma Generator for the NexION 1000/2000/5000 ICP-MS Systems, PerkinElmer Technical Note, 2020.

Consumables Used

Component/Description	Part Number
PFA ST3 Nebulizer with Integrated Gas Line	N8152378
Fixed 2.0 mm Injector UHP Quartz Torch	N8152428
SilQ Spray Chamber with AMS Gas Port	N8152539
Grey/Grey 1.30 mm I.D. Santoprene Peristaltic Pump Tubing	N8152415
Orange/Green Flared 2-Stop PVC Pump Tubing	N8145197
Gas Line- Matrix	N8152374

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