



APPLICATION NOTE

ICP - Mass Spectrometry

AUTHORS

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High Throughput Laser Ablation Analysis of REE Ore Samples Using the NexION 5000 ICP-MS Coupled to a LaserTRAX System

Introduction

Rare earth elements (REEs) are increasingly important in the production of high-specification electronic devices from smartphones, computer components, LEDs, catalysts in engines/petroleum

refinement, electric motors (automotive), and high-specification alloys. Annually, around 240 million tons of rare earth metals are produced with more than half (140M tons) originating from China, 30M tons from Myanmar, and large reserves from Vietnam, Russia and India, while smaller deposits in North America, Australia and sub-Saharan Africa are being assessed for economic viability. Discovery of REEs requires a rapid and cost-effective screening of survey samples for REE content, as greater resolution of a survey area would necessitate analysis of hundreds/thousands of samples per day.

Traditionally, inorganic analysis of geological survey samples requires acid digestion. Several different approaches of acid digestion could be required, depending on rock/mineral composition, which have time and safety implications, require large volumes of acid, and produce extensive chemical waste. A global push towards more sustainable operations with a smaller chemical footprint makes this approach unsuitable.

Many mining discovery samples are already routinely fused into beads for XRF analysis to determine bulk/major composition. Laser ablation (LA) of these fused beads would bypass the need for acid digestion and reduce waste and resource consumption. LA-ICP-MS was previously a low volume, labor-intensive technique; however, the LaserTRAX laser ablation sample introduction system from Elemental Scientific Lasers (ESL) coupled with PerkinElmer's NexION® 5000 Multi-Quadrupole ICP-MS¹ provides a unique combination of automated, fast sample-to-sample load times and precise analysis for both major and minor elements within these fused beads.

Experimental

Methodology

The NexION 5000 ICP-MS has many unique features that allow for the precise analysis of laser ablated samples and seamlessly interfaces with the LaserTRAX system via a simple push-fit connection. The powered interface controls and enhances the transport of ions into the ICP-MS for increased sensitivity, allowing for lower detection limits and improved accuracy for minor elements. However, the enhanced transport does not compromise the ability to measure major elements as the proprietary Extended Dynamic Range (EDR) capability selectively adjusts the degree of attenuation on a mass-by-mass basis. Plus, the NexION 5000's high duty cycle delivers a data acquisition rate of 100,000 points per second, while the presence of four gas channels combined with a Dynamic Reaction Cell (DRC) provides for superior interference removal.

For this application, the LaserTRAX was used to directly analyze XRF beads made from REE ore samples. The XRF beads are routinely produced and analyzed for bulk/major element composition of ores before they are sent for processing. The capability of being able to use the same beads for both XRF and LA-ICP-MS analysis cuts down on sample preparation and eliminates the need to use large amounts of acids, which has both human health and environmental benefits. LaserTRAX is a laser ablation instrument designed specifically for high-throughput, automated analysis of up to 1200 samples per day, with a 60-second analysis time per sample, and includes a robot for sample handling, a barcode scanner, and a laser ablation system, seamlessly connected to the NexION ICP-MS – in this case, a NexION 5000 Multi-Quadrupole ICP-MS. The parameters used for analysis on the LaserTRAX-NexION 5000 LA-ICP-MS solution are listed in Table 1.

Table 1: Parameters for LaserTRAX system and NexION 5000 ICP-MS.

	Parameter	Value
LaserTRAX	Laser Wavelength	193 nm
	He Sample Gas	0.8 L/min
	Fluence	8 J/cm ²
	Repetition Rate	20 Hz
	Spot Size	100 µm
NexION 5000	Plasma Flow	16 L/min
	Auxiliary Flow	1.2 L/min
	RF Power	1200 W
	Nebulizer	PFA
	Nebulizer Gas Flow	0.35-0.4 L/min (Tuned for 1.5% oxides)
	Spray Chamber	SIQ cyclonic
	Injector/Torch	SIQ one-piece torch with 2 mm injector
	Sample Flow Rate	0.8 L/min
	Cones	Pt (Sampler and Skimmer) Hyper-Skimmer with OmniRing used in extraction mode
	Analysis Mode	Reaction (DRC) with NH ₃ and Standard

Samples

The NexION 5000 ICP-MS was tuned for optimum sensitivity using a glass reference standard (NIST610). A U/Th ratio of 1 and a ThO/Th oxide ratio of less than 1% were obtained.

Blanks and standards consisted of a blank fused bead and five standards, which were matrix matched to the ores by fusing 0.25 g of the CRM OREAS 20a (not measured for in this experiment) into Li-tetraborate along with the standard and 1000 ppm Ta as an internal standard. OREAS 20a was used as it has a low concentration of REE elements but has the desired effect of having similar ablation characteristics as the samples analyzed in this work.

The samples were made by fusing 1.25 g of sample into a Li-tetraborate bead with a spiked Ta internal standard at a concentration of 1000 ppm. The samples consisted of six reference materials (Table 2) and 24 blank fusions that were included between the CRM samples to create a large batch size, with the blanks, standards and reference materials, bracketing these that were run in sequence 24 times. The sample-to-sample analysis time was on average 75 seconds, creating an analytical run in excess of 14 hours and consisting of approximately 700 analyses.

Table 2: CRM samples and sample matrix.

Sample	Rock Type
OREAS 25a	Soil
OREAS 100a	Uranium Bearing Ore
OREAS 101b	Uranium Bearing Ore
OREAS 106	High Grade Uranium Reference Material
OREAS 120	Uranium Ore
OREAS 124	Uranium Ore

Results and Discussion

CRM Recovery

Initially, all elements were measured in MS/MS Standard mode using correction equations where necessary, and percent recoveries determined for each reference sample. Table 3 shows the averaged recoveries of 27 measurements over a 14-hour run. Only recoveries for those elements within the calibration range are reported.

Most recoveries are within 10% of the given CRM values, with a few exceptions. However, the value for Gd is consistently low in the presence of high Ce (OREAS 100a, 100b, 106) (above 500 ppm).

Table 3: % Recovery of REEs in a range of rock reference standards prepared as Li-tetraborate fused discs.

Sample	Recovery %													
	La (139)	Ce (140)	Pr (141)	Nd (143)	Sm (147)	Eu (153)	Gd (155)	Tb (159)	Dy (163)	Ho (165)	Er (166)	Tm (169)	Yb (172)	Lu (175)
OREAS 25a	99%	95%		90%			94%		93%	99%	97%	99%	98%	98%
OREAS 100a	98%	98%	94%	90%	105%	104%	86%	99%	91%	99%	94%	103%	98%	103%
OREAS 101b		94%	88%	84%	89%	99%	85%	101%	86%	101%	90%	122%	95%	120%
OREAS 106	94%	101%	87%	91%	92%	92%	87%	90%	92%	97%	94%	95%	100%	100%
OREAS 120	110%	104%		106%		115%	103%		108%	112%	-		109%	
OREAS 124	101%	100%		97%		106%	96%		98%	101%	96%		103%	129%

The stability of analysis is shown in Figure 1, where the repeated recovery of 27 measurements of one of the CRM materials (OREAS 106) is plotted over a 14-hour analysis. It can be seen that all recoveries are within $\pm 20\%$, with most recoveries within 10%. The exception is Gd where the recoveries are more consistently low but still within the acceptable $\pm 20\%$, matching the earlier observation that recoveries for Gd are low in the presence of high Ce. This suggests that the interference of CeO on Gd is being overcorrected, especially when there is a high Ce content, thus requiring a more reliable interference correction by either removing the CeO interference or mass shifting the analyte of interest, Gd, away from the interference.

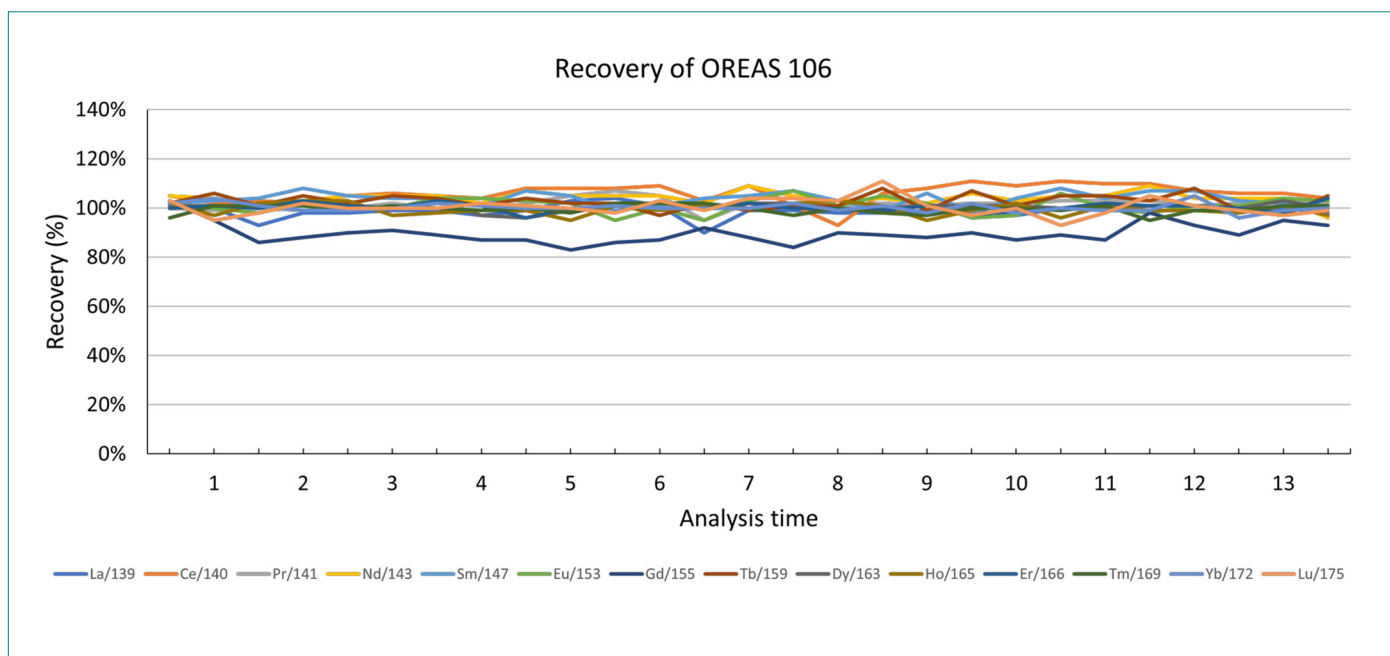


Figure 1: Recovery for REEs in OREAS 106 ore reference material over 27 replicates over a period of 14 hours.

Interference Corrections for Higher Level La and Ce Ores

When measuring REEs, it is common to use oxygen, as a cell gas, to remove the oxide interferences from light mass REEs on higher mass REEs, via a reaction with oxygen to form REEO_2^+ ions, away from the interferences. However, this strategy does not work when measuring Gd in the presence of Ce. The reason is that Gd^+ reacts with O_2 to form GdO^+ while CeO^+ (which to some extent is formed in the plasma) reacts with O_2 to create CeO_2^+ at several masses where GdO^+ ions reside.

However, the ability to use pure ammonia (NH_3) with the NexION 5000 ICP-MS allows Gd to be measured interference-free in Mass Shift mode. Gd^+ reacts with ammonia creating several $\text{GdNH}(\text{NH}_3)_x^+$ clusters (Figure 2), with the intensity of the cluster depending on the NH_3 flow. Sensitivity of the clusters at higher masses increases with a higher reaction gas flow (Figure 3), but CeO^+ does not react so readily, as shown in Figure 4. As a result, Gd can be measured interference-free at a variety of different masses where the $\text{GdNH}(\text{NH}_3)_x^+$ clusters are formed.

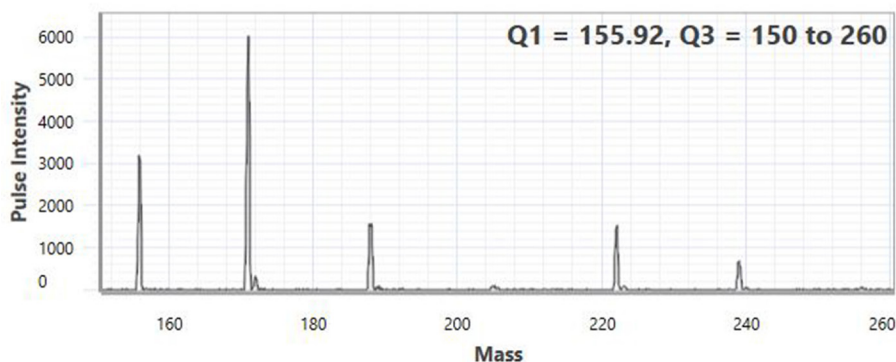


Figure 2: Product ion scan of 1 ppb Gd creating several $\text{GdNH}(\text{NH}_3)_x^+$ clusters with 0.4 mL/min of NH_3 flow.

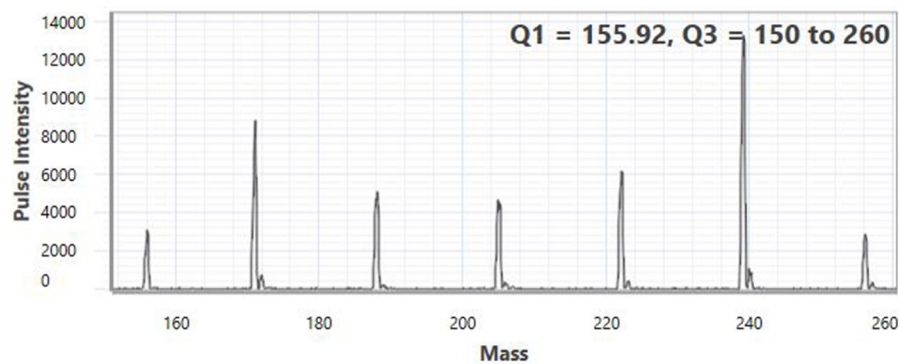


Figure 3: Product ion scan of 1 ppb Gd creating several $\text{GdNH}(\text{NH}_3)_x^+$ clusters with 0.6 mL/min of NH_3 flow.

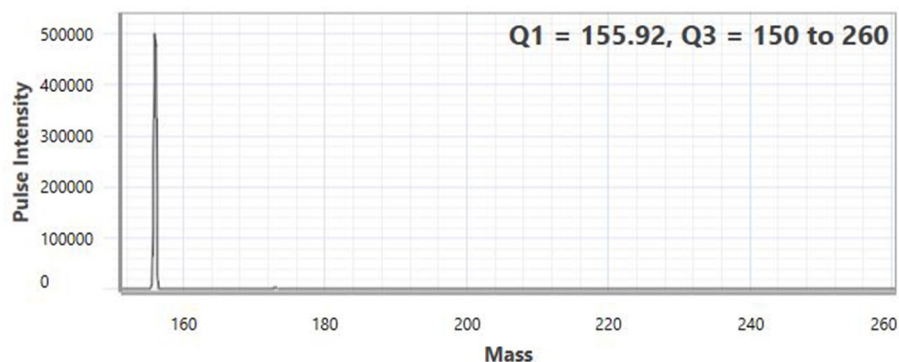


Figure 4: Product ion scan of 100 ppb CeO showing minimal reaction with NH_3 at 0.4 mL/min flow.

To assess the ability to analyze Gd in a high Ce matrix using Reaction mode with NH_3 , 1.25 g of a OREAS 20a reference material was spiked with 10,000 ppm Ce and fused into a bead to simulate a high-Ce REE ore. OREAS 20a was used due to the low levels of REE elements in the CRM, allowing the effect of the added Ce to be observed. NH_3 was introduced to the DRC cell and optimized to a flow rate for the best sensitivity for each cluster, as shown in the Figures 3 and 4. The recovery results of Gd for Standard mode versus two Gd NH_3 clusters, in the presence of high Ce, are shown in Table 4.

In this example, in Standard mode, with no addition of a reaction gas (i.e. Gd 156/156 in MS/MS mode), there was no correction equation added to remove the CeO interference from ^{156}Gd . In Table 4 (column 1), you can see from the results that for ^{156}Gd in Standard mode with no correction equation, the recovery exceeds 150%. In a real screening scenario, this would overestimate the Gd content on an ore, giving a false impression of economic viability.

The sample was re-analyzed using NH_3 in the DRC to mass-shift Gd away from the CeO interference (Table 4, columns 2 and 3), resulting in both ^{156}Gd and ^{158}Gd returning results < 10% from the certified value (n=3), an outcome that is reproducible over both short- and long-term analyses. This ensures that an accurate profile is determined for all REEs in each sample.

Table 4: Gd recovery in OREAS 20a spiked with 10,000 ppm Ce.

	Gd 156/156 MS/MS	Gd 156/171 Mass Shift	Gd 158/173 Mass Shift
Measured Conc (ppm)	12.1	6.32	6.71
Certified Conc (ppm)	6.78	6.78	6.78
% Recovery	178 %	93 %	99 %
Precision	0.67%	1.21%	1.13%

Conclusion

In conclusion, a LaserTRAX laser ablation sample introduction system coupled to the NexION 5000 Multi-Quadrupole ICP-MS allowed for the direct analysis of thousands of fused beads per day with no need for acid digestion. In many cases, the fused beads have already been produced for XRF analysis, so LaserTRAX vastly improves the efficiency of the sample preparation workflow, with recoveries in the $100\% \pm 10\%$ range for screening of REE-bearing ores.

The NexION 5000 ICP-MS was shown to be an ideal tool for this analysis, allowing for major elemental analysis using Extended Dynamic Range capabilities and reliable, controlled reactions for the best interference removal. The NexION is a sensitive and robust detector suitable for the routine quantification of ultra-trace impurities and major components in solid matrices, with the ability to rapidly switch to Reaction with O_2 and NH_3 modes to resolve analytical issues.

The interference removal described here is simple to apply, performs well throughout the analyte/interference concentration range and is, therefore, suitable for use in a high-throughput workflow environment.

References

1. "LaserTRAX-NexION 5000 ICP-MS - Your Fully Automated Sample Introduction, Laser Ablation Solution", PerkinElmer Flyer, 2022.