

Analysis of Geological Materials for Rare Earth Elements on the PlasmaQuant® MS Elite

1. SUMMARY

In recent years, there has been a rising demand for rare earth elements (REEs) in the fields of user electronics, catalysis, optical displays, high-performance magnets, batteries, aerospace manufacturing and medical applications. Hence, there is the need for reliable trace analysis procedures in the assessment of potential mining sites, process control solutions (largely comprising of rare earth oxides, REO) and quality control of high-purity REEs. Furthermore, there is a large interest in academic research in earth sciences involving trace and ultra-trace level determination of REEs in geology, geochemistry and mineralogy.

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) is a popular analytical technique in the determination of REEs, from raw materials including soils, rocks and ores to impurities in highly refined rare-earth products.

The technique offers fast, multielement detection of REE at concentrations down to the parts-per-quadrillion (ppq) range. However, challenges often faced by scientists in the measurement of REE include the occurrence of polyatomic and isobaric interferences that are not resolved by quadrupole ICP-MS. Sample preparation can also impose some analytical constraints and must be considered in order to obtain accurate and precise analytical data.



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REEs commonly suffer from polyatomic interferences that result from the formation of oxides and hydroxides of other REEs or from other matrix elements typically present in geological samples, like Barium (Table 1). This is particularly important for REEs such as Pr, Tb, Ho and Tm that have only one stable isotope available for measurement. Therefore, an effective interference management system is essential in removing polyatomic interferences and also negates the need for traditional mathematical correction of polyatomic interferences.

Within this study the PlasmaQuant® MS Elite was used to analyze five geological reference materials, including rock, stream sediment, shale, basalt and cement, regarding their REE content using the Integrated Collision Reaction Cell (iCRC) to remove polyatomic interferences.

2. INSTRUMENTATION

A PlasmaQuant® MS Elite ICP-MS in combination with a Cetac ASX-520 autosampler was used for the sample analysis. The instrument comprises the ReflexION – a patented 3D focusing ion optics system that provides exceptionally high sensitivity of more than 1500 million counts/second per milligram/Liter (part per million) of analyte (^{115}In), while maintaining oxide formation (CeO^+/Ce^+) at below 2%. Furthermore, the PlasmaQuant® MS Elite is equipped with the patented integrated Collision Reaction Cell (iCRC) to remove polyatomic species formed in the plasma and greatly improve the precision and accuracy of an analysis. All experiments were carried out in a routine analytical laboratory, and not under 'clean room' conditions. The method parameters were optimized using the ASpect-MS software's auto-optimization routine to automatically optimize all ion optics, nebulizer, and plasma parameters. The total sampling time, including the rinse and sample uptake delays, was approximately two minutes per sample. The operating conditions are summarized in Table 2.

Table 1: REE isotope mass, abundance and potential polyatomic interference

| Isotope | Abundance | Polyatomic interference |
|-------------------|-----------|---|
| ^{139}La | 99.9 | |
| ^{140}Ce | 88.5 | |
| ^{141}Pr | 100 | |
| ^{144}Nd | 23.8 | |
| ^{146}Nd | 17.3 | |
| ^{147}Sm | 15.1 | |
| ^{151}Eu | 47.8 | $^{135}\text{Ba}^{16}\text{O}$ |
| ^{159}Tb | 100 | $^{143}\text{Nd}^{16}\text{O}$ |
| ^{160}Gd | 21.9 | $^{144}\text{Nd}^{16}\text{O}$ |
| ^{163}Dy | 25 | $^{146}\text{Nd}^{16}\text{O}^1\text{H}$, $^{147}\text{Sm}^{16}\text{O}$ |
| ^{165}Ho | 100 | $^{149}\text{Sm}^{16}\text{O}$ |
| ^{167}Er | 22.9 | $^{150}\text{Sm}^{16}\text{O}^1\text{H}$, $^{151}\text{Eu}^{16}\text{O}$ |
| ^{169}Tm | 100 | $^{152}\text{Sm}^{16}\text{O}^1\text{H}$ |
| ^{174}Yb | 31.8 | $^{158}\text{Gd}^{16}\text{O}$ |
| ^{175}Lu | 97.4 | $^{159}\text{Tb}^{16}\text{O}$, $^{158}\text{Gd}^{16}\text{O}^1\text{H}$ |

Table 2: Instrument settings – PlasmaQuant® MS Elite

| Parameter | Settings |
|---------------------|---|
| Plasma Gas Flow | 9.0 L/min |
| Auxiliary Gas Flow | 1.35 L/min |
| Nebulizer Gas Flow | 0.97 L/min |
| iCRC Gas Setting | No gas mode; Gas mode with 100 mL/min He |
| Plasma RF Power | 1.30 kW |
| Dwell Time | 30 ms |
| Scans per Replicate | 10 (peak hopping, 1pt/peak) |
| No. of replicates | 5 |
| Pump Rate | 8 rpm - black/black PVC pump tubing |
| Sample uptake time | 30 s |
| Stabilization delay | 20 s |
| Ion Optics | Auto-optimized for highest sensitivity |

3. REAGENTS AND SAMPLES

The following high purity reagents were used for all solution preparations:

- Deionized water (>18.2 MΩ/cm, Millipore MilliQ)
- Nitric acid Supra-quality 69% (ROTIPURAN[®] Supra)
- Sodium peroxide (Na₂O₂) finely powdered, reagent grade, 97% (SIGMA-ALDRICH[®])

Calibration standards

Calibration solutions were prepared from high-purity, single and multi-element solutions (SIGMA-ALDRICH[®]) in 1% HNO₃ + 1.2 g of Na₂O₂ covering the concentration range from 0.25 to 25 µg/L for La, from 0.5 to 50 µg/L for Ce and Nd and from 0.05 to 5 µg/L to Pr, Sm, Eu, Gd, Tb, Dy, Er, Ho, Tm, Yb and Lu.

Sample preparation

For the quantification of REEs, it is important that complete digestion of the sample is achieved because any insoluble residue will result in an underestimated concentration of these elements. When acid mixtures containing hydrofluoric acid (HF) are used, insoluble fluorides of REEs may remain in the precipitate. In fact, refractory minerals such as zircon, tourmaline, chromite, rutile, garnet, spinel and corundum are incompletely decomposed by an acid attack. Decomposition by lithium metaborate and tetraborate fusion provides a complete decomposition of silicate phases and accessory minerals, however, results in a higher amount of total dissolved solids (TDS). Since ICP-MS is typically limited to TDS levels of less than 0.2%w/v, the fusion decomposition requires additional dilution prior to analysis. For several types of geological matrices, sintering with Na₂O₂ is a very attractive analytical decomposition procedure because it is highly effective in decomposing minerals rapidly and the resulting sinter residue is easy to dissolve. Additionally, it does not introduce high concentrations of reagent elements (eg. Li, B) that may affect future analyses¹.

Therefore, a sintering digestion in the presence of Na₂O₂ was considered within this study. Approximately 100 mg of sample grounded to pass a 200-mesh sieve was well mixed with 600 mg of Na₂O₂ and sintered at 480 ± 10 °C for exactly 30 minutes in a Carbolite muffle furnace (CWF 1200) using porcelain crucibles (30 x 30 mm²) lined with aluminum sheet. After cooling, the sinter residue was gently removed from the crucible with ultra-pure water added dropwise into a 50 ml polypropylene tube. When the reaction finished, 3 drops of concentrated HCl and 2 ml of concentrated HNO₃ were added. The tube was filled to the mark with ultrapure water and the final solution was homogenized using a vortex stirrer. Before analysis, the solution was diluted ten-fold with 1% HNO₃.

Internal standard

An internal standard solution of 1 µg/L In and Ir in 1% HNO₃ was added online to the sample solution via a Y-connector using an additional channel on the peristaltic pump.

4. RESULTS AND DISCUSSION

The formation of polyatomic species such as MO⁺ and MOH⁺ is greatly influenced by the chemical nature of the respective element. Since oxide and hydroxide formation will follow particular stoichiometric reactions, their contribution to an analyte signal can be corrected by a fixed numerical coefficient (correction equation) determined for the specific analysis conditions. Cerium has a strong affinity for oxygen with oxide levels of less than 2% being typically under optimized instrument conditions. Oxide interferences can be significantly reduced to negligible levels without the need for correction equations by injecting a Helium gas at a flow rate of 100 mL/min into the iCRC interference management system (Figure 1).

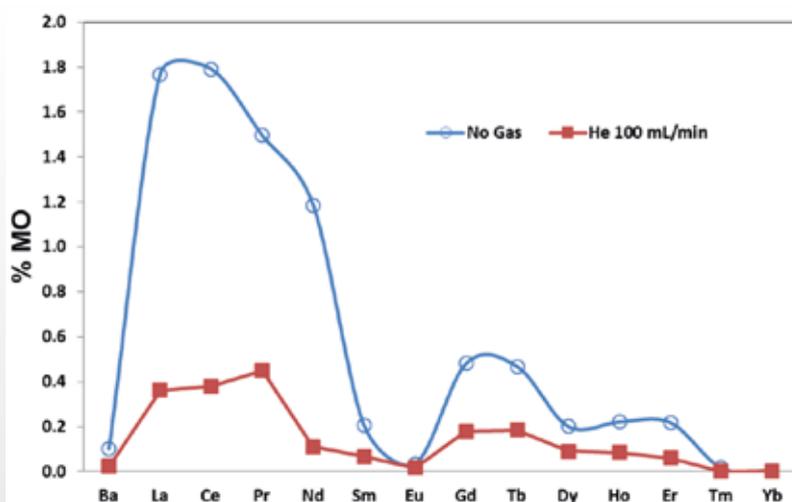


Figure 1: Oxide formation in different iCRC modes determined from single element standards

Z-scores

The Z-score parameter was adopted to evaluate the analytical quality of measured values (Figure 2). It was calculated according to the organization criteria for laboratories operating to pure geochemistry fitness-for-purpose², using the following equation:

$$Z = \frac{(X - X_a)}{h_a}$$

with Z being the Z-Score, X the measured concentration, X_a the target concentration and h_a the target precision. A satisfying result is defined to be within the threshold Z-score of ±2.

Within the scope of this study, five certified reference materials (CRM), three from the geological proficiency testing program (GeoPT) and two Chinese soil CRMs were investigated. The reference materials are listed in Table 3.

Table 3: Investigated CRMs

| Name | Type | Name | Type |
|------------|--------|-------------------|-----------------|
| GeoPT CRMs | | Chinese soil CRMs | |
| HTB-1 | Basalt | GBW 7103 | Rock |
| OPC-1 | Cement | GBW 7359 | Stream sediment |
| SBC-1 | Shale | | |

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The CRMs were investigated with and without Helium used as a collision gas within the iCRC. No corrections for oxide and hydroxide polyatomic interferences were made, although isobaric interferences were accounted for.

Figure 2 displays the Z-score results for all investigated geological samples under both conditions. The results depicted in Figure 2b represent the obtained values in collision gas mode, while Figure 2a are those obtained without gas. The Z-score values are well within the ± 2 threshold and demonstrate the accuracy of the applied method in terms of applied digestion procedure and the effectiveness of the iCRC interference management system to remove polyatomic interferences.

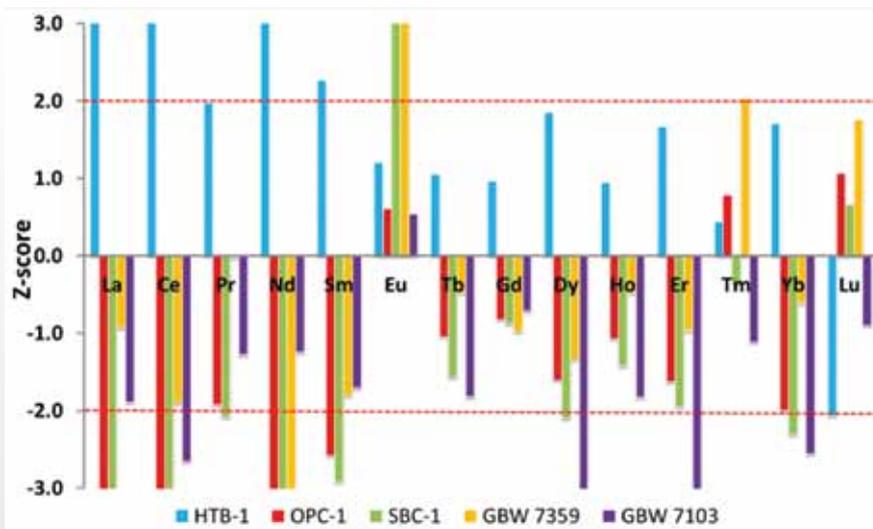


Figure 2a: Z-score without iCRC gas. The red dotted lines indicate the $\pm 2\sigma$ threshold.

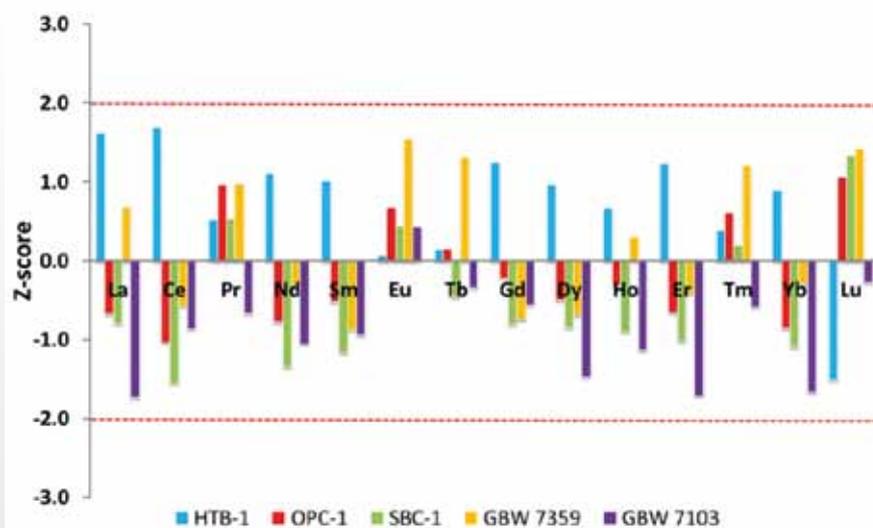


Figure 2b: Z-score with iCRC gas (100 mL/min He gas flow). The red dotted lines indicate the $\pm 2\sigma$ threshold.

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Shown in Tables 4 and 5 are the measured concentration values of REEs in each of the investigated certified reference materials using iCRC with Helium collision gas. Concentrations range from µg/kg to mg/kg and excellent recoveries were achieved, again verifying the accuracy of the method as established by the Z-scores.

Table 4: Comparison of measured and certified values for HTB-1, OPC-1 and SBC-1

| Element | HTB-1 (Basalt) | | | OPC-1 (Cement) | | | SBC-1 (Shale) | | |
|-------------------|----------------|-----------|-------------|----------------|-----------|-------------|---------------|-----------|-------------|
| | Measured | Certified | %Recovery | Measured | Certified | %Recovery | Measured | Certified | %Recovery |
| | mg/kg | | | | | | | | |
| ¹³⁹ La | 43.9 | 40.9 | 107% | 26.7 | 25.9 | 103% | 54.3 | 52.5 | 103% |
| ¹⁴⁰ Ce | 97.6 | 91.3 | 107% | 51.1 | 48.9 | 104% | 114.8 | 108.2 | 106% |
| ¹⁴¹ Pr | 12.2 | 11.9 | 103% | 5.83 | 6.20 | 94% | 12.2 | 12.6 | 97% |
| ¹⁴⁴ Nd | 53.9 | 51.4 | 105% | 25.6 | 24.7 | 104% | 52.1 | 49.2 | 106% |
| ¹⁴⁷ Sm | 11.6 | 11.0 | 106% | 4.65 | 4.50 | 103% | 10.25 | 9.62 | 107% |
| ¹⁵¹ Eu | 3.36 | 3.35 | 100% | 0.95 | 1.00 | 95% | 1.92 | 1.98 | 97% |
| ¹⁵⁹ Tb | 1.55 | 1.53 | 101% | 0.51 | 0.52 | 98% | 1.27 | 1.23 | 104% |
| ¹⁶⁰ Gd | 11.0 | 10.3 | 107% | 3.80 | 3.75 | 101% | 8.94 | 8.54 | 105% |
| ¹⁶³ Dy | 8.87 | 8.4 | 106% | 2.97 | 2.87 | 103% | 7.46 | 7.1 | 105% |
| ¹⁶⁵ Ho | 1.68 | 1.6 | 105% | 0.57 | 0.55 | 104% | 1.45 | 1.36 | 107% |
| ¹⁶⁷ Er | 4.44 | 4.14 | 107% | 1.59 | 1.52 | 105% | 4.04 | 3.79 | 107% |
| ¹⁶⁹ Tm | 0.57 | 0.55 | 103% | 0.20 | 0.21 | 95% | 0.55 | 0.56 | 98% |
| ¹⁷⁴ Yb | 3.67 | 3.46 | 106% | 1.43 | 1.34 | 107% | 3.90 | 3.64 | 107% |
| ¹⁷⁵ Lu | 0.42 | 0.49 | 86% | 0.18 | 0.20 | 90% | 0.48 | 0.54 | 88% |

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Table 5: Comparison of measured and certified values for GBW 7103 and GBW 7359

| Element | GBW 7103 (Rock) | | | GBW 7359 (Sediment) | | |
|-------------------|-----------------|-----------|-------------|---------------------|-----------|-------------|
| | Measured | Certified | %Recovery | Measured | Certified | %Recovery |
| | mg/kg | | | | | |
| ¹³⁹ La | 60.9 | 54 | 113% | 13.2 | 13.9 | 95% |
| ¹⁴⁰ Ce | 114.0 | 108 | 106% | 25.1 | 24.0 | 105% |
| ¹⁴¹ Pr | 13.2 | 12.7 | 104% | 2.61 | 2.90 | 90% |
| ¹⁴⁴ Nd | 51.2 | 47 | 109% | 9.94 | 9.80 | 101% |
| ¹⁴⁷ Sm | 10.6 | 9.7 | 108% | 1.99 | 1.90 | 105% |
| ¹⁵¹ Eu | 0.82 | 0.85 | 96% | 0.57 | 0.62 | 92% |
| ¹⁵⁹ Tb | 1.68 | 1.65 | 102% | 0.26 | 0.29 | 90% |
| ¹⁶⁰ Gd | 9.69 | 9.3 | 104% | 1.77 | 1.70 | 104% |
| ¹⁶³ Dy | 10.8 | 10.2 | 106% | 1.77 | 1.70 | 104% |
| ¹⁶⁵ Ho | 2.24 | 2.05 | 109% | 0.32 | 0.33 | 97% |
| ¹⁶⁷ Er | 7.01 | 6.5 | 108% | 0.97 | 0.93 | 104% |
| ¹⁶⁹ Tm | 1.11 | 1.06 | 105% | 0.14 | 0.16 | 88% |
| ¹⁷⁴ Yb | 8.23 | 7.4 | 111% | 1.03 | 1.00 | 103% |
| ¹⁷⁵ Lu | 1.17 | 1.15 | 102% | 0.13 | 0.16 | 81% |

Method Detection Limits (MDL)

Method detection limits in the original solid sample were calculated from three times the standard deviation of ten blank measurements in the presence of Na₂O₂ matrix on the basis of the applied digestion procedure and dilution factors, including the addition of helium collision gas into the iCRC (Table 6).

Table 6: Three sigma method detection limits

| Element | Method Detection Limits / $\mu\text{g kg}^{-1}$ | Element | Method Detection Limits / $\mu\text{g kg}^{-1}$ |
|---------|---|---------|---|
| | (iCRC Helium mode) | | (iCRC Helium mode) |
| La | 3.5 | Gd | 1.4 |
| Ce | 0.9 | Dy | 0.4 |
| Pr | 0.6 | Ho | 1.6 |
| Nd | 2.6 | Er | 0.3 |
| Sm | 2.7 | Tm | 0.8 |
| Eu | 2.7 | Yb | 1.5 |
| Tb | 0.8 | Lu | 0.4 |

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5. CONCLUSION

The PlasmaQuant® MS Elite was successful in determining the concentrations of REE in different geological certified reference materials after performing a sintering digestion with Na₂O₂. From the Z-score analysis, it can be concluded the iCRC interference management system effectively removes polyatomic interferences and allows for the accurate and precise measurement of REEs without pre-defined correction equations. At the same time, the high sensitivity allows very low method detection limits in the ng/kg to µg/kg range to be routinely achieved.

Acknowledgements

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References

- [1] T. Meisel et al., *Geostandard Newslett* 2002, 26, 53-61.
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