

Challenge

Determination of REE in geological materials down to the parts-per-quadrillion (ppq) range

Solution

Simple and reliable method using PlasmaQuant MS Elite without need for traditional mathematical correction of polyatomic interferences

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

Introduction

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.

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.

Materials and Methods

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	Specification
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

Samples and reagents

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

- Deionized water (> 18.2 MΩ cm, Millipore MiliQ)
- Nitric acid Supra-quality 69% (ROTIPURAN® Supra)
- Sodium peroxide (Na_2O_2) finely powdered, reagent grade, 97% (SIGMA-ALDRICH®)

Calibration

Calibration solutions were prepared from high-purity, single and multi-element solutions (SIGMA-ALDRICH) in 1% HNO_3 + 1.2 g of Na_2O_2 covering the concentration range from 0.25 to 25 $\mu\text{g/L}$ for La, from 0.5 to 50 $\mu\text{g/L}$ for Ce and Nd and from 0.05 to 5 $\mu\text{g/L}$ 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 Na_2O_2 is a very attractive analytical decomposition procedure

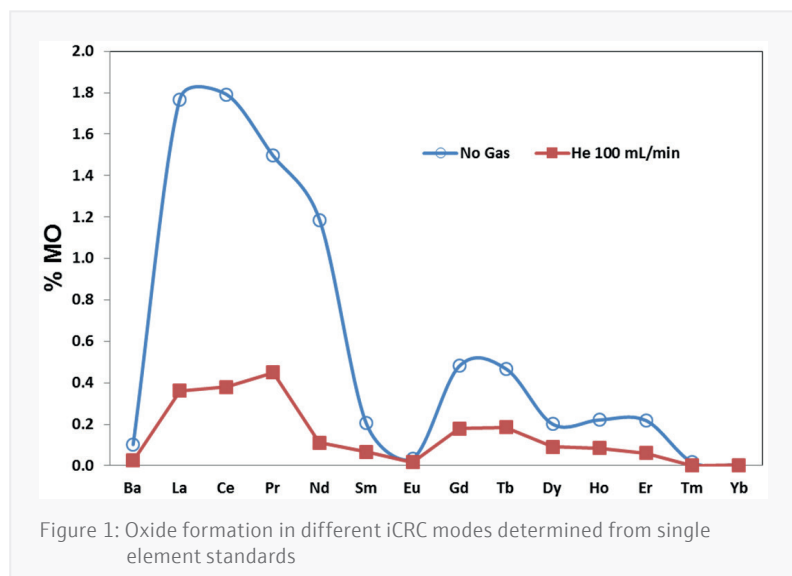
because it is highly effective in decomposing minerals rapidly and the resulting sinter residue is easy to dissolve. Additionally, it does not introduce high concentrations of reagent elements (eg. Li, B) that may affect future analyses¹.

Therefore, a sintering digestion in the presence of Na_2O_2 was considered within this study. Approximately 100 mg of sample ground to pass a 200-mesh sieve was well mixed with 600 mg of Na_2O_2 and sintered at 480 ± 10 °C for exactly 30 minutes in a Carbolite muffle furnace (CWF 1200) using porcelain crucibles (30 x 30 mm) 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, three drops of concentrated HCl and 2 mL of concentrated HNO_3 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% HNO_3 .

An internal standard solution of 1 $\mu\text{g/L}$ In and Ir in 1% HNO_3 was added online to the sample solution via a Y-connector using an additional channel on the peristaltic pump.

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).



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.

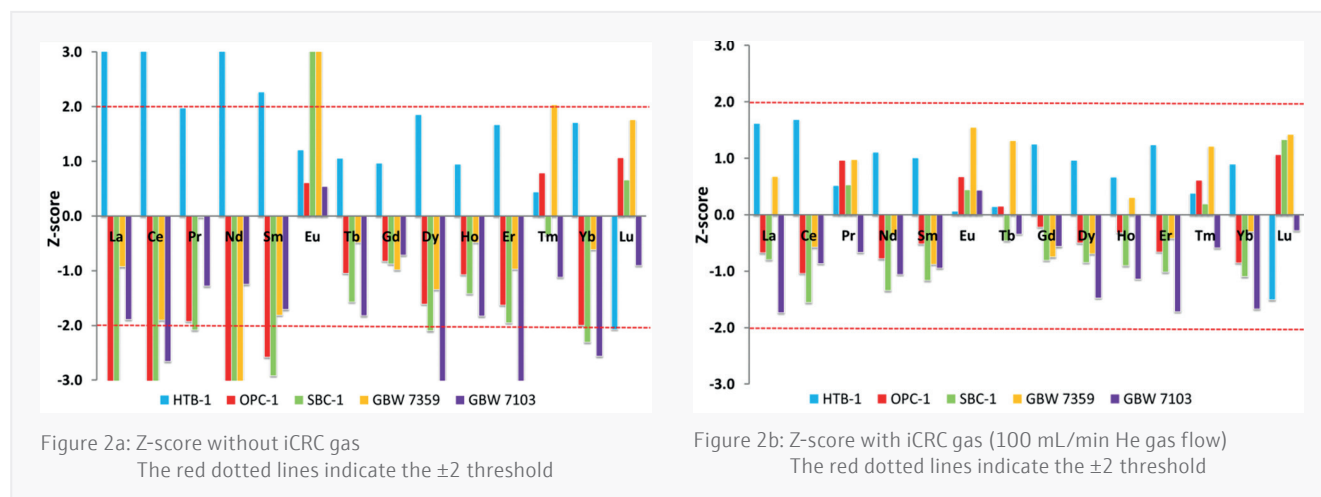
Within the scope of this study, five certified reference materials (CRM), three from the geological proficiency testing program (GeoPT) and two Chinese soil CRMs were investigated. The reference materials are listed in Table 3.

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		

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.



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%

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 Na_2O_2 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/ $\mu\text{g kg}^{-1}$		
	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

Summary

The PlasmaQuant MS Elite was successful in determining the concentrations of REE in different geological certified reference materials after performing a sintering digestion with Na_2O_2 . 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 $\mu\text{g/kg}$ range to be routinely achieved.



Figure 2: PlasmaQuant MS Elite

References

- [1] T. Meisel et al., *Geostandard Newslett* 2002, 26, 53-61.
 [2] M. Thompson, et al., *Geostandard Newslett* 1999, 23, 87-121.

Acknowledgements

Analytik Jena GmbH wants to thank the Geological Survey of Portugal (LNEG) for performing the digestion procedure of the investigated geological reference materials.

Headquarters

Analytik Jena GmbH+Co.KG
 Konrad-Zuse-Strasse 1
 07745 Jena · Germany

Phone +49 3641 77 70
 Fax +49 3641 77 9279

info@analytik-jena.com
 www.analytik-jena.com

Version 2.1 · Author: RS
 en · 06/2024

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