

Article

Rare Earth Elements Determination by Inductively Coupled Plasma Mass Spectrometry after Alkaline Fusion Preparation

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Abstract: There is an increasing worldwide demand for rare earth elements (REEs) in new technological applications—such as electronics, superconductors, space applications, etc. The determination of low concentration REEs in geological samples is extremely important since they are the source materials for all REE products. In order to improve the accuracy and precision of REE measurements by inductively coupled plasma mass spectrometry (ICP-MS); complete digestion of refractory phases and minerals in the samples, low procedural blanks, separation of interfering matrix, and elimination of interference on the mass of the analytes of interest must be fulfilled. Conventional methods that use a hotplate and a mixture of four acids are effective but can take time to achieve complete dissolution of samples that contain highly refractory phases, which is unacceptable in the mining and metallurgical industry. Such difficult samples necessitate high-temperature alkaline flux fusion as it offers a faster and more efficient alternative to acid digestion. This paper presents an accurate, precise, rapid, and reliable method for rare earth element analysis by ICP-MS with low detection limits, which involves no sample pre-concentration, and is therefore able to deliver data rapidly. The analytical performance of the developed method was tested successfully on various REE rock-type certified reference materials and evaluated statistically. The results obtained were in reasonable agreement with published certificate values.

Keywords: rare earth elements; ICP-MS; geological; low LODs; accuracy; precision



Citation: Mnculwane, H.T. Rare Earth Elements Determination by Inductively Coupled Plasma Mass Spectrometry after Alkaline Fusion Preparation. *Analytica* **2022**, *3*, 135–143. <https://doi.org/10.3390/analytica3010010>

Academic Editor: Konstantinos Simeonidis

Received: 30 January 2022

Accepted: 2 March 2022

Published: 18 March 2022

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1. Introduction

The rare earth elements (REE) are a group of 17 metallic elements which appear in the periodic table. The group consists of the 15 lanthanide elements (which are: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu)) as well as yttrium (Y) and scandium (Sc). Their physical and chemical characteristics are so similar that, for many years, it was very difficult to separate these elements from each other and quantify them. In the last 50 years, methods have been developed to achieve separation and precise determination of all the REEs, even when these elements are present at trace levels.

The worldwide demand for REE is steadily increasing for new technology applications such as electronics, optoelectronics, superconductors, super-magnets, lasers, computers, rechargeable hydride batteries, artificial diamonds, glass and ceramics, space applications, etc. Some of the world's most exotic and innovative technologies that play a significant role in our day-to-day life owe their success to rare earths. Although REE are present in low concentrations in most minerals (over 190 minerals containing significant amounts of REE), the primary resources of REE are only three minerals—namely, bastnaesite, monazite, and xenotime. The determination of REE in geological and metallurgical samples is extremely important because they are the source materials for all REE products.

In order to improve the accuracy and precision of REE, Sc, and Y measurements by ICP-MS, the following conditions must be fulfilled:

1. Complete digestion of refractory phases and minerals in the samples;
2. Low procedural blanks;
3. Separation of interfering matrix;
4. Elimination of molecular (i.e., oxides and hydrides) and direct isobaric interferences on the mass of the analytes of interest.

Complete dissolution of refractory minerals (such as zircon, garnet, cassiterite, tourmalines, chromite, and others) is a prerequisite for accurate and precise elemental analysis of these geological and metallurgical materials with solution-based ICP-MS. Conventional methods that use hotplate or high-pressure Parr Bombs and a mixture of HCL- HNO₃-HF HClO₄ [1,2] are effective but can take days to achieve complete dissolution of samples that contain highly refractory phases which is unacceptable in the mining and metallurgical industries. Such difficult samples therefore necessitate high-temperature alkaline flux fusion, because it offers a faster and more efficient alternative to acid digestion.

Alkaline fusion also eliminates the need for multiple evaporation and acid conversion steps, which are commonly required in acid dissolution protocols and can potentially result in incomplete sample dissolution, contamination, or elevated blank levels. Large quantities of fusion salts added cause depression of the analyte signal intensity, clogging of the nebuliser, deposition on the orifice of the sampler cone, and drift in the analyte signal [3]. For several types of geological matrices, fusing with Na₂O₂ was a very attractive analytical decomposition procedure, because it is highly effective in attacking minerals quickly and the resulting residue is easy to dissolve, additionally it does not introduce elements that cause significant memory effects [4–6] and lower TDS compared to other fusion salts combinations, especially when a lower sample aliquot is utilised.

The fusion procedure is normally followed by a pre-concentration step that is obviously time consuming, leading to analysis turnaround issues. Other methods include precipitation of the REEs with sodium hydroxide to remove aluminium and alkaline earth metals; precipitation with hydrochloric acid to remove iron, titanium, zirconium and other elements forming soluble fluorides; and chlorination to remove elements that form volatile chlorides including iron, titanium, aluminium, and zirconium. Various procedures for the REE determination have been based on combinations of these separation procedures, but they usually incur significant loss of REEs amounting to 3–25% [3].

Recently, inductively coupled plasma spectrometry (ICP) has become a widely used technique for rare earth element determination because of good specificity, precision, and accuracy, low detection limits, wide linear dynamic range with minimal sample matrix effects and simple operation [7–12]. It is possible to analyse samples of widely different chemical and mineralogical compositions without the need for preliminary separation or pre-concentration of REEs [13].

The aim of this investigation was to develop an accurate, precise, rapid, and reliable ICP-MS method suitable for routine REE analysis, with the objective to accelerate the fusion technique and increase its capacity. The refined procedure involved a straight-forward sodium peroxide fusion in a preheated furnace and dilution of sample with no attended pre-concentration chemistry. The method was developed with emphasis on the importance of complete sample dissolution, appropriate matrix dilution, and control of polyatomic interferences. This work documents the efficiency of the protocol by presenting its performance evaluated using several rare earth certified reference materials (CRMs).

2. Materials and Methods

2.1. Reagents, Standard Solutions, and Certified Reference Materials

Nitric acid 65% (*w/w*) analytical grade, ACS, ISO grade sodium peroxide, sodium hydroxide (Merck), single-element standard solutions 1000 mg/L of In, Re, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y ICP grade AccuStandard were purchased from Stargate (Johannesburg, South Africa). Ultrapure water (18.2 MΩ cm) was prepared with Milli-Q system Type 1 water (Merck) which was used throughout the experiments. Certified reference materials (CRMs), CGL111 and CGL124, are from Mongolia Central

geological laboratory which are monazite and xenotime respectively; the OREAS100a was from OREAS, Australia.

2.2. Sample Preparation, Preparation of Calibration Standards, and Instrumentation

Individual 0.2000 g of samples (CRMs) were weighed into 10 mL zirconium crucibles and 2.0000 g of dry Na₂O₂ and 2 pellets of NaOH were added and thoroughly mixed with the sample. The crucibles were placed into a pre-heated muffle furnace at 600 °C for 45 min. The crucibles were removed from the furnace, cooled down, and thereafter placed into 250 mL beakers containing 10 mL ultrapure water plus a pinch of tartaric acid to catalyse dissolution. Leach with 5 mL HNO₃ and quantitatively transfer samples into 50 mL volumetric flasks and filled up to the mark with ultrapure water. Reagent blanks—containing only acids, salts, and ultrapure water, without samples—were prepared the same way as samples. The content of REEs in the obtained solutions was measured by ICP-MS (Perkin Elmer 300Q NexION) under the instrumental conditions presented in Table 1. After instrument warm-up, a daily performance test was measured where sensitivity was monitored using indium isotope (¹¹⁵In > 30000 cps) and the oxide interference levels were monitored using cerium oxide and controlled at ¹⁵⁶CeO < 0.5% using a 1 ppb set-up standard, if successful; then, the instrument was deemed ready for REE analysis. The daily performance test for the ICP-MS instrument was the most critical especially in REE determination, because it was reported and proven to keep oxide/hydroxide interferences at minimal or insignificant levels [14,15].

Table 1. NexION-ICP-MS operating and measurement conditions for the determination of REEs.

Parameter	Actual Value
Nebuliser gas flow	0.82 L/min
Auxiliary gas flow	1.3 L/min
Plasma gas flow	15 L/min
RF Power	1300 W
Analog pulse voltage	−2331
Pulse stage voltage	1000
Double charge: Ce ⁺⁺ /Ce ⁺	≤0.03
Oxide levels; CeO ⁺ /Ce ⁺	≤2.5%
Internal STDs	¹⁸⁷ Re and ¹¹⁵ In
Sampler and skimmer cones	Nickel

Calibration of the instrument was performed with three multi-element standards of different elements from single element standard solutions covering the REE entire spectrum of isotope, tabulated in Table 2. Isobaric interferences were corrected on the software using standard mathematical equations. In order to correct for possible non-spectral interferences, 0.01 mg/L (Re and In) was used as the internal standard and the standard solutions were prepared in 2% (v/v) HNO₃ to match the final sample acid matrix. The reagent blank solution and quality control (QC) sample spiked with a known concentration were also prepared in 2% (v/v) HNO₃ and 0.01 mg/L Re and In. The calibration standards were also matrix-matched with the samples. The calibration curves for the individual elements were strategically constructed as shown in Table 2, with emphasis on avoiding light-REE interfering with heavy-REE in terms of oxides formation in the calibration standards; hence, LREE standards were prepared separately from the HREE. Another consideration covered in the calibration strategy was the natural abundance and occurrence of REE in their ores in terms of concentration content (i.e., LREE was always higher in ratio compared to HREE and therefore calibrated accordingly).

Table 2. Calibration standards in mg/L prepared for REE analysis by ICP-MS.

Element	Isotope /Mass	STD1	STD2	STD3	STD4	STD5	STD6	STD7	STD8	STD9	STD10	STD11	STD12	STD13	STD14	STD15
Y	89	0.05	0.10	0.20	0.60	1.0	0.01 mg/L internal standard									
In	115															
La	139	0.20	1.0	3.0	5.0	8.0										
Ce	140	0.20	0.40	1.0	5.0	12										
Pr	141	0.05	0.10	0.20	0.60	1.0										
Nd	146	0.20	1.0	3.0	5.0	8.0										
Sm	147	0.05	0.10	0.20	0.60	1.0										
Eu	151						0.01	0.05	1.0	0.50	1.0					
Tb	159						0.01	0.05	1.0	0.50	1.0					
Gd	160						0.01	0.05	1.0	0.50	1.0					
Dy	163											0.01	0.05	1.0	0.50	1.0
Ho	165											0.002	0.006	0.04	0.08	0.1
Er	167											0.002	0.006	0.04	0.08	0.1
Tm	169											0.002	0.006	0.04	0.08	0.1
Yb	174											0.002	0.006	0.04	0.08	0.1
Lu	175											0.002	0.006	0.04	0.08	0.1
Re	187	0.01 mg/L internal standard														

2.3. Method Validation

Method validation was performed by evaluating the linearity, accuracy, and precision, which included repeatability and reproducibility, limit of detection (LOD), limit of quantification (LOQ), and specificity/selectivity. The performance criteria is stipulated in Table 3.

Table 3. Criteria for REE method acceptance.

Performance Parameter	Criteria
Selectivity/specificity	Isotopes must be free from interferences or corrected for
Repeatability	RSD < 5% for concentrations above 100 ppm RSD < 10% for concentrations below 100 ppm
Reproducibility	RSD < 5% for concentrations above 100 ppm RSD < 15% for concentrations below 100 ppm
Accuracy or recoveries	Recoveries of check solutions must be within: 10%
Calibration linearity	Must have correlation of 0.99 to 1
Limits of detection	Must be generally above the blank reading
Limits of quantification	Must be clearly above blank reading

3. Results and Discussions

3.1. Demonstration of Selectivity, Sensitivity, Linearity, and Range

The simplest calibration procedure requires preparation of a series of standard solutions from the reference solution, by dilution of a stock solution, covering a reasonable range of signal response from the instrument. The sensitivity of the ICP-MS technique was demonstrated by the gradient of the calibration response curve, as presented in Figure 1. Selectivity is the degree to which the method can quantify the target analyte in the presence of other analytes, matrices, or other potentially interfering materials, and this parameter was manifested on by the linearity of the calibration curve for each individual element. Linearity is depicted by the correlation coefficient (R^2), see Figures 1 and 2. Linear ranges may be different for different matrices and, for this reason, the working range in this work was kept within the respective individual standard calibration range to avoid any possible effect of interference inherent from the matrix.

3.2. Limits of Detection (LOD) and Limits of Quantification (LOQ)

LOD and LOQ for each element are listed in Table 4 as evaluated on the NexION-ICP-MS. The LOD and LOQ were based on the amount of the analyte which yielded a signal equivalent to 3- and 10-times the standard deviation of the background and were calculated using the most abundant isotope of each element, respectively (see Equations (1)–(4)). The determined LOD and LOQ indicated the dependence and reliability on the ICP-MS instrument used in the determination of REEs.

$$\text{LOD} = (3 \times \% \text{RSD}_B \times \text{BEC}) / 100, \quad (1)$$

$$LOQ = (10 \times \%RSD_B \times BEC)/100, \tag{2}$$

$$SBR = (STD_{intensity} - Av.B_{intensity})/Av.B_{intensity}, \tag{3}$$

$$BEC = STD_{concentration}/SBR, \tag{4}$$

where $\%RSD_B$ is the percentage relative standard deviation of 10-times blank responses, SBR is signal background ratio, BEC is background equivalent concentration, $STD_{intensity}$ and $STD_{concentration}$ are intensity and concentration of any standard in the calibration respectively, and $Av.B_{intensity}$ is the average of 10-times blank responses.

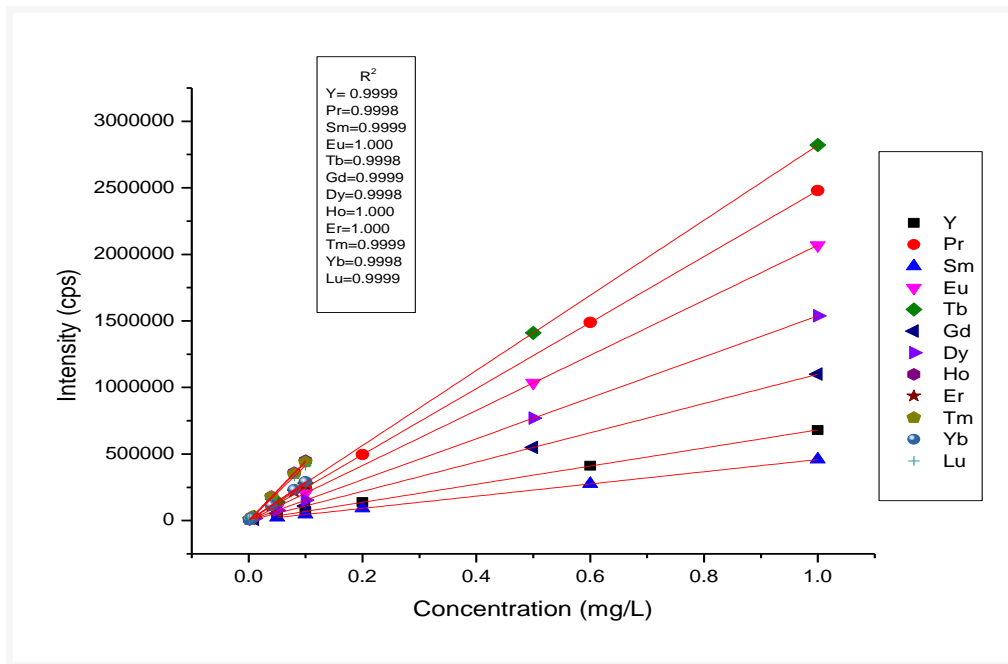


Figure 1. Regression plots obtained for HREEs at various concentration ranges.

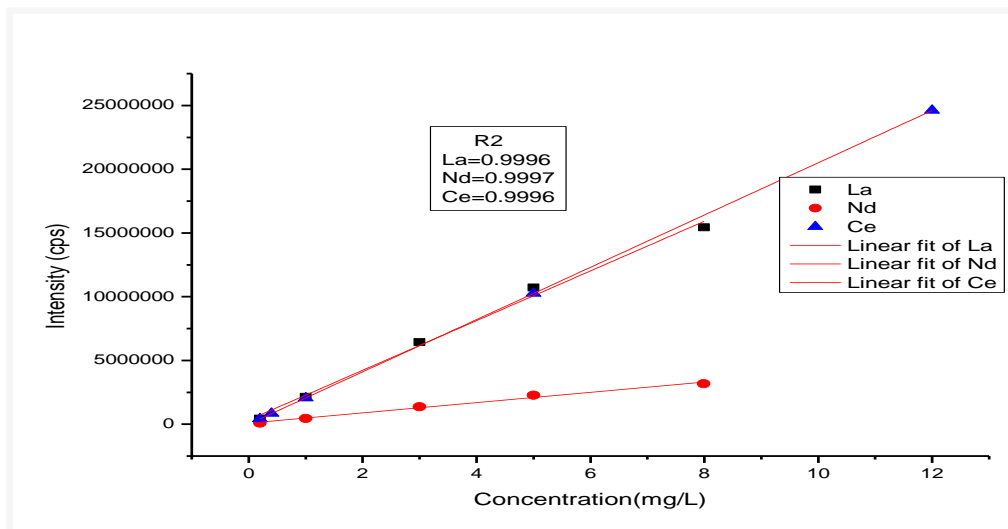


Figure 2. Regression plots obtained for LREEs at various concentration ranges.

Table 4. Limits of detection (LOD) and quantification (LOQ) as evaluated on the 300Q Perkin Elmer ICP-MS.

BLK	n	LOD mg/L	LOQ mg/L
89Y	10	0.00282	0.00939
139La	10	0.00887	0.02955
140Ce	10	0.01563	0.05211
141Pr	10	0.00167	0.00555
146Nd	10	0.00617	0.02058
147Sm	10	0.00095	0.00318
151Eu	10	0.00021	0.00071
159Tb	10	0.00021	0.00071
160Gd	10	0.00131	0.00438
163Dy	10	0.00057	0.00192
165Ho	10	0.00012	0.00041
167Er	10	0.00026	0.00087
169Tm	10	0.00004	0.00012
174Yb	10	0.00020	0.00066
175Lu	10	0.00004	0.00013

3.3. Repeatability and Reproducibility

Repeatability is the type of precision that refers to the degree of agreement of results when conditions are maintained as constant as possible with the same analyst, reagents, equipment, and instruments performed within a short period of time. It is commonly demonstrated by the standard deviation of simultaneous duplicates or replicates. As shown in Table 5, the quality control (QC) sample gave acceptable recoveries that fall within the range of 95–105% with an RSD of less than 5%. The REE data obtained from the QC sample demonstrated excellent precision and accuracy of the method.

Table 5. Repeatability and stability evaluated REE quality control sample.

QC STD	Average mg/L	n	SD mg/L	%RSD	Expected mg/L	% Recovery
89Y	0.098	10	0.0022	2.24	0.100	98
139La	0.995	10	0.0054	0.54	1.000	100
140Ce	0.999	10	0.0079	0.79	1.000	100
141Pr	0.205	10	0.0015	0.73	0.200	103
146Nd	0.995	10	0.0047	0.47	1.000	100
147Sm	0.207	10	0.0108	5.22	0.200	104
151Eu	0.202	10	0.0014	0.69	0.200	101
159Tb	0.197	10	0.004	2.03	0.200	99
160Gd	0.209	10	0.012	5.74	0.200	105
163Dy	0.205	10	0.0145	7.07	0.200	103
165Ho	0.04	10	0.0003	0.75	0.040	100
167Er	0.041	10	0.0004	0.98	0.040	103
169Tm	0.042	10	0.0006	1.43	0.040	105
174Yb	0.039	10	0.0015	3.85	0.040	98
175Lu	0.041	10	0.0004	0.98	0.040	103

3.4. Reproducibility, Accuracy, and Precision

On the other hand, reproducibility is the type of precision that refers to degree of agreement of results when a variety of conditions are as different as possible with the different analyst, reagents, equipment, and instruments performed over an extended period of time, expressed as %RSD. In this work, the validation criterion was evaluated on three different certified reference material samples that presented different sample matrices, by different analysts, over different days. Reproducibility is not defined separately from ruggedness, as it caters deliberate variations to the method, hence these were covered simultaneously.

Certified reference materials samples (CRMs) can address all aspects of bias (method, laboratory, and run bias); they are defined with a statement of uncertainty and traceable to international standards. CRMs are therefore considered as useful tools to achieve traceability in analytical measurements, to calibrate equipment and methods (in certain cases), to monitor laboratory performance, to validate methods, and to allow comparison of methods [16,17].

Accuracy of an analytical method may be defined as the closeness of agreement between test results and the accepted reference value. The aim of the method is to estimate the true value of the analyte concentration with an uncertainty that is fit for purpose. However, in such analytical methods, the analyte is transferred from the complex matrix to a simpler solution, whereby there is a loss of analyte. As a consequence, the measured value will be lower than the true concentration present in the original matrix [18]. The percentage of recovery of the reference values calculated, as the ratio between laboratory results and reference values, is an effective way to evaluate the accuracy of the data [19]. In fact, analyte losses during the decomposition step, matrix influence in quantification step, and even the correction coefficient efficiency for minimisation of polyatomic interferences may be studied in a semi-quantitative approach.

Three well-characterised CRMs (CGL11, CGL124, and OREAS100a) covering three of the most representative geological ores or matrices, were used in this work, for the evaluation of the method's performance in the REE determination. In Tables 6–8, analytical data (average of 10 replicates) and some statistic parameters obtained for these samples were presented. The data are also presented graphically in Figure 3. Comparative REEs data presented in the tables validated a comment on the accuracy and precision of the analyses in evaluation of the developed method's performance.

Table 6. Performance of the developed method on CGL111 analysis in terms of accuracy and precision.

CGL111	Ce	Dy	Er	Eu	Gd	Ho	La	Nd	Pr	Sm	Tb	Y	Yb
Average	29,812	197	83.2	215	512	39.7	18,834	8484	2762	895	50.9	939	58.2
Acc. value	29,000	206	80.0	212	553	37.0	19,300	8900	2800	900	55.0	959	55.0
Recovery (%)	103	96	104	101	93	107	98	95	99	99	93	98	106
SD	620	9.0	7.9	9.3	20.3	2.1	510.2	230.4	71.7	55.1	3.2	37.7	1.6
RSD	2.1	4.6	9.5	4.3	4.0	5.3	2.7	2.7	2.6	6.2	6.3	4.0	2.7

Table 7. Performance of the developed method on CGL124 analysis in terms of accuracy and precision.

CGL124	Ce	Dy	Er	Eu	Gd	Ho	La	Nd	Pr	Sm	Tb	Y	Yb
Average	28,944	58.1	23.1	89.6	274	8.2	22,066	6532	2425	524	47.2	177	18.1
Acc. value	27,600	58.0	24.0	87.0	295	8.0	21,100	6500	2300	539	45.0	167	18.0
Recovery (%)	105	100	96	103	93	103	105	100	105	97	105	106	101
SD	997	4.5	1.4	3.6	16.0	0.1	162.6	38.6	23.0	6.6	3.8	5.0	0.9
RSD	3.4	7.7	6.0	4.0	5.8	1.2	0.7	0.6	1.0	1.3	8.0	2.8	4.7

Table 8. Performance of the developed method on OREAS100a analysis in terms of accuracy and precision.

OREAS100a	Ce	Dy	Er	Eu	Gd	Ho	La	Lu	Nd	Pr	Sm	Tb	Tm	Y	Yb
Average	437	19.1	12.7	3.9	21.0	3.8	240	1.6	142	43.8	23.9	3.0	1.8	90.5	10.7
Acc. value	467	18.9	11.6	3.7	20.3	3.7	259	1.6	152	47.1	23.8	3.3	1.6	95.5	11.4
Recovery (%)	94	101	109	107	103	105	93	105	93	93	100	92	111	95	94
SD	35	0.7	1.2	0.4	0.5	0.2	22.2	0.2	6.5	3.1	1.2	0.3	0.2	3.9	1.0
RSD	8.0	3.8	9.1	9.9	2.5	5.6	9.3	10.0	4.6	7.0	4.8	9.1	9.6	4.3	9.4

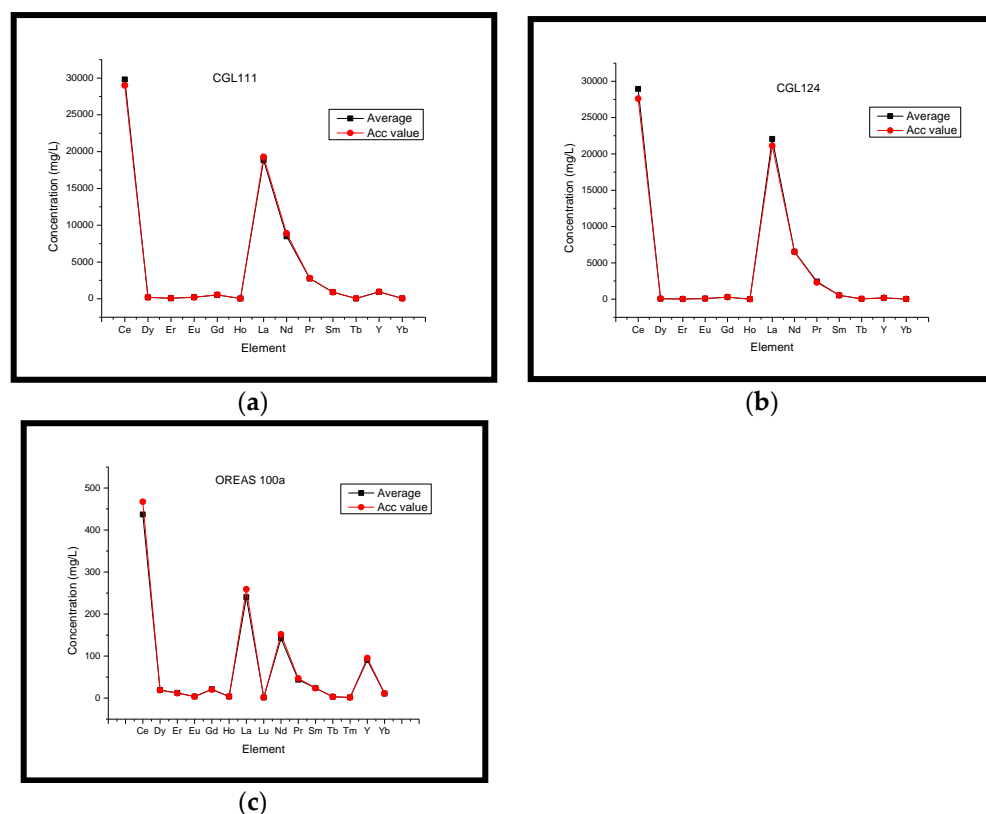


Figure 3. Evaluation of the method's performance in the REE determination: (a) CGL 111; (b) CGL 124; (c) OREAS 100a.

In terms of accuracy of the method, for most of the quantified REEs, recoveries varying between 90% and 110% have been achieved in all the three analysed CRMs. REE data for the international standards that had been tested in this work were in agreement with the published certificate values for the CRMs.

With respect to precision, relative standard deviation (RSD) values lower than 5% were achieved for most elements with the described method in this study. These values were evenly distributed and almost independent of REE concentrations. In fewer cases, poorer precisions were obtained at lower concentration level measurements, close to the methodology quantification limits, an RSD of about 15% can be expected.

4. Conclusions

The capabilities of the developed methodology for the quantification of REEs were fully explored by analysing a variety of different types of geological matrices. The improved protocol for REE determination in geological samples using ICP-MS has been demonstrated to be reliable and fit for intended purpose, as all criteria in Table 3. The results of appropriate analytical quality were obtained in most of the CRMs investigated.

The alkaline fusion preparation ensured rapid, efficient, and fairly inexpensive decomposition, as it required no pre-concentration steps with the advantage of reduced sample preparation time, resulting in greater sample throughput when compared to the classical methods involving pre-concentration steps and hand fusion.

The use of geological reference materials was revealed to be an essential tool to evaluate the performance degree of several options that have been made and, therefore, to achieve a validated robust methodology.

The ICP-MS as the final determination technique for rare earth analysis showed good sensitivity and sufficiently low detection limits, wide dynamic range, and the capability of accurate multi-element analysis, hence validating its fitness for the purpose.

Funding: This research was funded by MINTEK.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All relevant data are provided within this manuscript.

Conflicts of Interest: The author declares no conflict of interest.

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