AN APPLICATION REPORT FROM
SPECTRO ANALYTICAL INSTRUMENTS

XRF-155

SPECTRO XEPOS (XEP05)

Analysis of Rare Earth Elements (REE) Using the SPECTRO XEPOS ED-XRF

Introduction

Rare earth elements (REEs) have unique physical and chemical properties that make them essential for many modern technologies, such as magnets, catalysts, batteries, lasers, displays, and sensors. However, REEs are also scarce and unevenly distributed in the Earth's crust (illustration 1), making their extraction and processing challenging and costly. Therefore, it is important to develop accurate and efficient methods for the analysis of REEs in various materials, such as ores, concentrates, alloys, and waste streams.

Energy dispersive X-ray fluorescence (ED-XRF) is a method that can be used for the analysis of REEs. It can provide qualitative and quantitative information about the elemental composition of a sample, including the REEs, without the need for sample preparation or chemical separation. ED-XRF has several advantages over other techniques, such as lower cost, higher speed, and simpler operation.

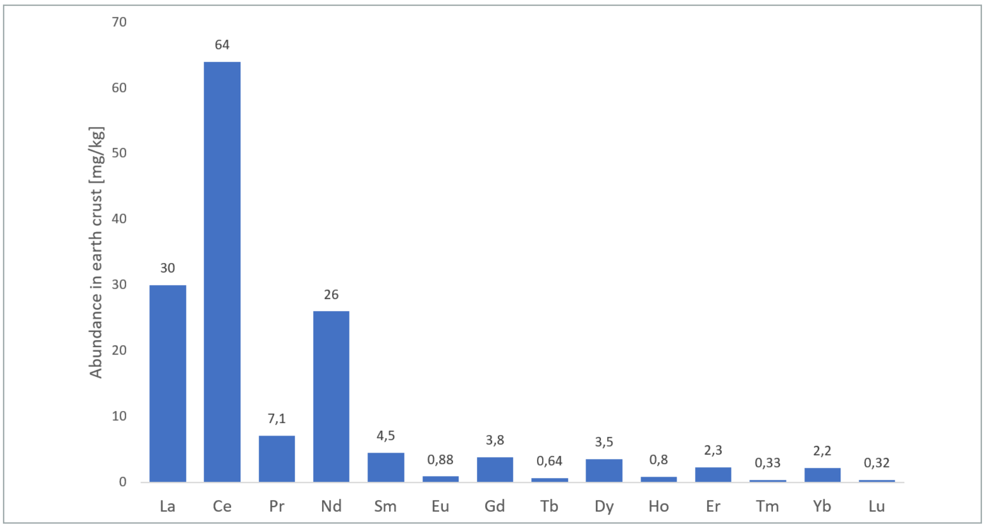

Illustration 1: Abundance of REE in the Earth's crust; reproduced from Wall (Critical metals handbook, chapter 13, 2014)

Instrumentation

The samples were excited for 1200 s by a 60 kV air-cooled low power thick binary Pd/Co alloy anode end window X-ray tube combined with an innovative monochromator, which also polarizes the primary tube spectrum. Additionally, the bandpass filter excitation is utilized for achieving monochromatic Co-excitation.

The illustration 2 shows the schematic setup of this adaptive excitation principle inside the SPECTRO XEPOS ED-XRF instrument. The main benefit for these monochromatic excitations is the boost in sensitivity for the analysis of the light elements Na-Cl as well as the elements K-Mn and Nd-Eu.

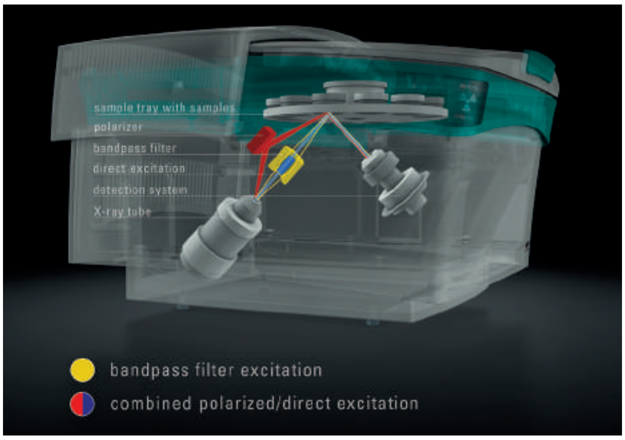

Illustration 2: Instrument schematics showing the adaptive excitation

A high resolution SDD was used to record the fluorescence radiation from the sample. The resolution for the SDD used was ≤130 eV for the Mn-Kα-line. The primary and secondary radiation paths in the instrument were flushed with helium for powder analysis. The components are packaged in a compact bench top housing with a small footprint. All measurement parameters stated below are controlled by the system PC and the XRF Analyzer Pro software.

Table 1: Measurement parameters of the SPECTRO XEPOS

Element Range	kV	Mode	Measurement Time
Na – Cl	17.5 kV	Polarisation	300 s
K – Mn, Nd – Sm	22.5 kV	Bandpass Filter	300 s
Fe – Mo, Gd – U	45.0 kV	Direct excitation	300 s
Ru – Pr	60.0 kV	Direct excitation	300 s

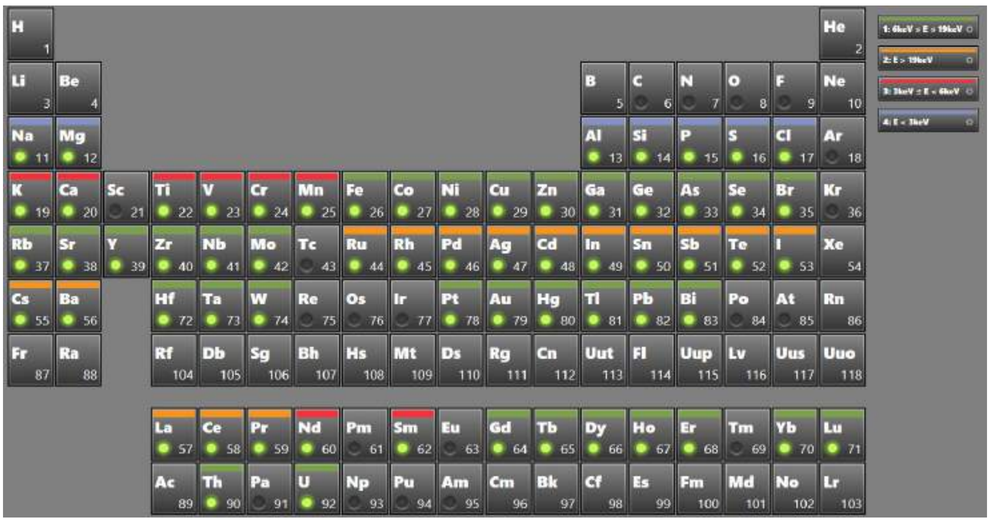

Illustration 3: Periodic table of the elements with assignment of measurement conditions

Samples

For the application described in this report, powders of certified reference materials were used. In addition to standard geological reference samples the list of materials included the following rare earth ores: AMIS-0185, CGL-124, GBW 07158 – GBW 07161, GBW 07185 – 07186 & 07188, OREAS 460, 462 & 464. The samples GBW 07187 and OREAS 461 were analyzed as validation samples.

Sample Preparation

For preparation of the pressed pellets 5 g of powder were blended with 1 g of binder and pressed into steel rings with outer diameter of 40 mm and inner diameter of 32 mm.

Calibration

The calibration is based on measurements of the above mentioned reference samples. The analysis results were calculated using a fundamental parameters program for fluorescence and scattering with focus of trace element analysis (Geochem Traces) which is also a matrix independent screening method.

The following graphs show as examples the correlation for some REE oxides like La_2O_3, CeO_2, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, and Gd_2O_3 in samples prepared as pressed pellets, proving the good linearity. These correlation graphs also show the analysis results of the validation samples.

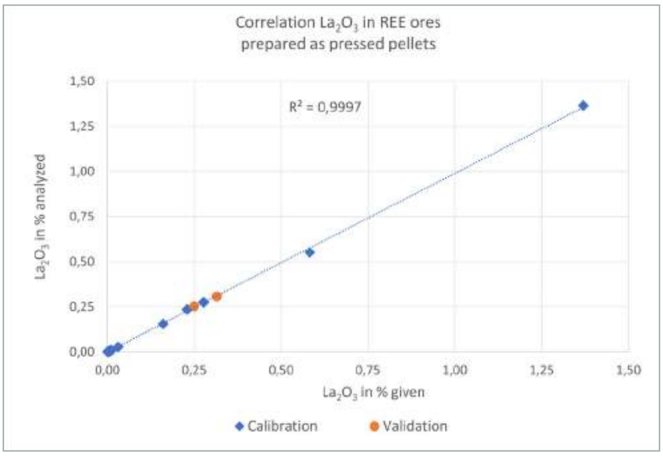

Figure 1: Correlation plot for La_2O_3

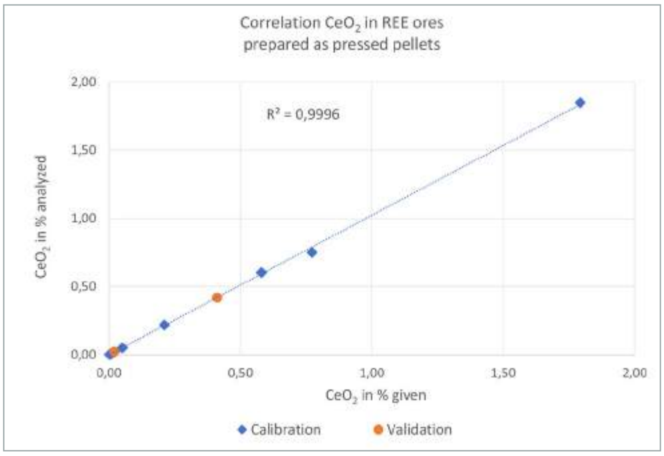

Figure 2: Correlation plot for CeO_2

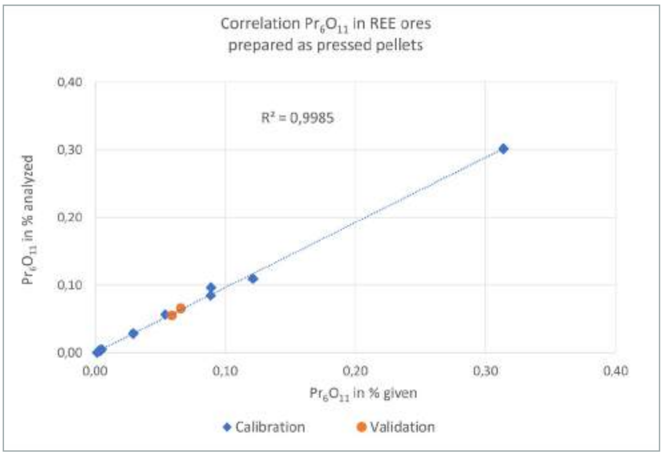

Figure 3: Correlation plot for Pr_6O_{11}

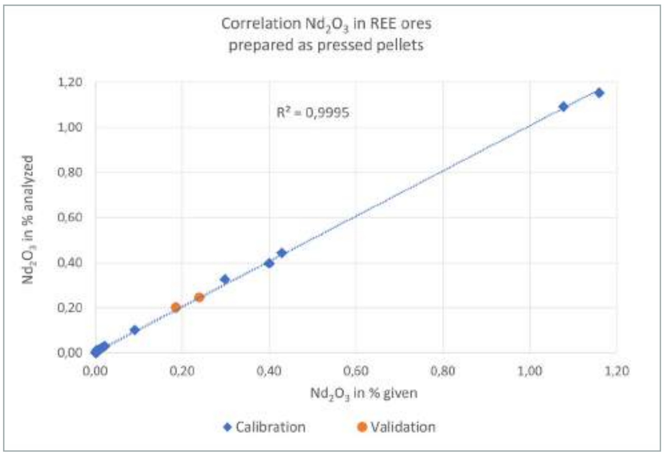

Figure 4: Correlation plot for Nd_2O_3

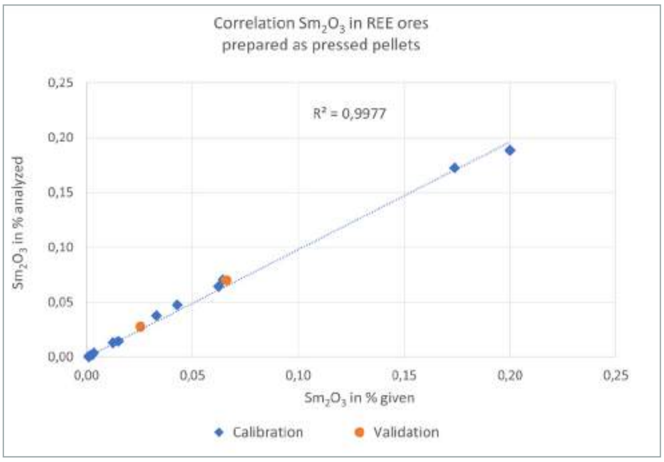

Figure 5: Correlation plot for Sm_2O_3

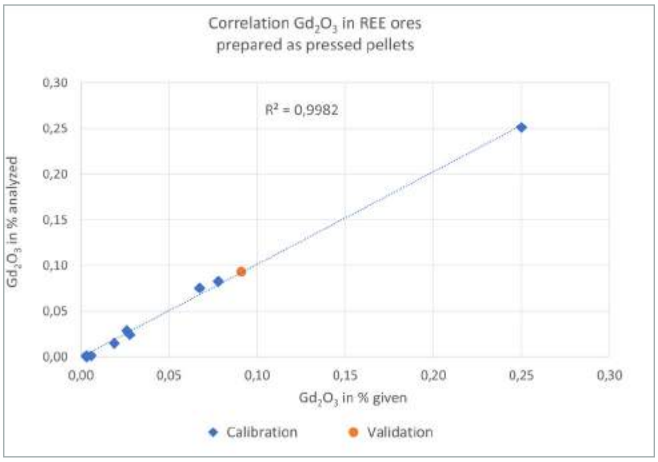

Figure 6: Correlation plot for Gd_2O_3

Limit of Detection

The below stated limits of detection were calculated based on pure SiO_2 powder matrix with a measurement time of 1200 seconds (300s per measurement condition) following the formula on the right. The LODs obtainable in real REE ore samples can be significantly higher and will depends on the concentrations of other elements like Fe.

Element	Limit of Detection (LOD)
La [mg/kg]	<3
Ce [mg/kg]	<3
Pr [mg/kg]	<2
Nd [mg/kg]	<2
Sm [mg/kg]	<2
Gd [mg/kg]	<3.5
Tb [mg/kg]	<3.2
Dy [mg/kg]	<3
Ho [mg/kg]	<3
Er [mg/kg]	<3
Yb [mg/kg]	<2

$$LOD = 3 * C_0 \frac{\sqrt{B}}{N}$$

N: Counts of an element specific line of a standard within a ROI having a width of 1,1*FWHM

B: Background behind the line within the same ROI

C_0: Concentration of the observed element in the standard

Table 2: REE's limit of detection in pure SiO_2 matrix

Results

The validation sample GBW 07187 was analyzed 10 times. The following table shows the analysis results of this repeatability test and compares the results to those of the certificate.

Table 3: Results overview for repeated analysis of validation sample GBW 07187

	La_2O_3 [%]	CeO_2 [%]	Pr_6O_{11} [%]	Nd_2O_3 [%]	Sm_2O_3 [%]	Gd_2O_3 [%]
Meas. 1	0.2572	0.02158	0.0667	0.2446	0.0694	0.0915
Meas. 2	0.2573	0.02087	0.0664	0.2451	0.0694	0.0932
Meas. 3	0.2584	0.02115	0.0669	0.2444	0.0695	0.0920
Meas. 4	0.2568	0.02119	0.0669	0.2445	0.0695	0.0930
Meas. 5	0.2569	0.02118	0.0669	0.2447	0.0699	0.0929
Meas. 6	0.2586	0.02209	0.0672	0.2445	0.0700	0.0929
Meas. 7	0.2585	0.02154	0.0672	0.2447	0.0698	0.0936
Meas. 8	0.2569	0.02132	0.0673	0.2449	0.0698	0.0942
Meas. 9	0.2584	0.02167	0.0669	0.2444	0.0695	0.0934
Meas. 10	0.2592	0.02194	0.0674	0.2448	0.0697	0.0924
Certified	0.25 ± 0.01	0.021 ± 0.002	0.066 ± 0.005	0.24 ± 0.01	0.066 ± 0.006	0.091 ± 0.002
Average	0.2578	0.0215	0.0670	0.2447	0.0696	0.0929
Min	0.2568	0.0209	0.0664	0.2444	0.0694	0.0915
Max	0.2592	0.0221	0.0674	0.2451	0.0700	0.0942
SD	0.0009	0.0004	0.0003	0.0002	0.0002	0.0008
Rel SD	0.30%	1.70%	0.40%	0.10%	0.30%	0.80%

	Tb_4O_7 [%]	Dy_2O_3 [%]	Ho_2O_3 [%]	Er_2O_3 [%]	Yb_2O_3 [%]	Lu_2O_3 [%]
Meas. 1	0.0177	0.1238	0.0240	0.06944	0.05225	0.0076
Meas. 2	0.0184	0.1248	0.0224	0.06934	0.05195	0.0077
Meas. 3	0.0171	0.1240	0.0244	0.06891	0.05247	0.0076
Meas. 4	0.0179	0.1232	0.0227	0.06956	0.05269	0.0076
Meas. 5	0.0164	0.1240	0.0225	0.06939	0.05311	0.0076
Meas. 6	0.0185	0.1238	0.0232	0.06952	0.05297	0.0077
Meas. 7	0.0172	0.1233	0.0227	0.06954	0.05248	0.0079
Meas. 8	0.0187	0.1247	0.0224	0.06924	0.0522	0.0077
Meas. 9	0.0191	0.1264	0.0227	0.06921	0.05235	0.0074
Meas. 10	0.0167	0.1231	0.0233	0.07018	0.05317	0.0079
Certified	0.019 ± 0.001	0.12 ± 0.01	(0.023)	0.068 ± 0.002	0.051 ± 0.003	0.0065 ± 0.0005
Average	0.0178	0.1241	0.023	0.0694	0.0526	0.0077
Min	0.0164	0.1231	0.0224	0.0689	0.052	0.0074
Max	0.0191	0.1264	0.0244	0.0702	0.0532	0.0079
SD	0.0009	0.0010	0.0007	0.0003	0.0004	0.0001
Rel SD	4.70%	0.80%	2.80%	0.50%	0.80%	1.90%

Summary

The SPECTRO XEPOS, equipped with the adaptive excitation and up to 60 kV excitation energy, is very well suited for the analysis of rare earth elements (REE), especially those ones excited using their K-lines. It proves to be an accurate and efficient instrument for the analysis of REEs as shown here for the analysis of REE ores. Compared to other techniques the analysis does not require any intensive sample preparation.

For some of the REEs, the analysis is quite limited due to rather low concentrations in nature and also due to possible line overlaps by major/minor elements like iron.

In view of size, power and cost the SPECTRO XEPOS meets the requirements of modern laboratories.

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