

Analytical Capabilities of EDXRF for Determination of Rare Earth Elements

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Abstract: Rare earth elements (REE) are present in the lanthanide range and are widely used in high-tech and clean technology applications that are predicted to grow significantly in the coming decades. Therefore, there will be a high demand for REE in the future that will impact the needs for development of sensitive and selective methods for determination of REEs such as X-Ray Fluorescence (XRF). Reliability of REEs analysis results depend on analytical capability of XRF instrument's performance. Analytical capability shows the ability of the instrument to perform sample analysis with high accuracy and precision and proven by validation so that the results obtained are reliable. The aim of this study is to assess the analytical capability of XRF for REEs analysis in samples particularly Lanthanum (La), Cerium (Ce), Neodymium (Nd), Samarium (Sm) and Yttrium (Y), by performing method validation of energy dispersive x-ray spectrometers (ED-XRF). Four measurement conditions that covered the selected elements were defined. Accuracy, precision and detection limits determination were performed by measuring the CRM In House Monazite Sand. The yield of the selected element corresponds to its certified value, with a %recovery between 95.99 to 103.1%. The %RSD values ranging from 0.59 to 5.19%. The detection limits (LLD) of ED-XRF ranged from 8.78 to 67.4 ppm. The results showed the good analytical capability of ED-XRF method for REEs analysis.

INTRODUCTION

The rare earth element (REE) is categorized as a metal and is found in the lanthanide series. The International Union of Pure and Applied Chemistry (IUPAC) describes REE, also identified as rare earth metal (REM) as one of seventeen chemical elements in the periodic table, consisting of fifteen lanthanides as well as scandium and yttrium. The 17 REEs are yttrium (Y), ytterbium (Yb), thulium (Tm), terbium (Tb), scandium (Sc), samarium (Sm), promethium (Pm), praseodymium (Pr), neodymium (Nd), lanthanum (La), holmium (Ho), gadolinium (Gd), europium (Eu), erbium (Er), dysprosium (Dy), lutetium (Lu) and cerium (Ce) (1). The lanthanide elements divided by electron shell configuration into light REE (LREE; La to Gd) and heavy REE (HREE; Tb to Lu) that has different characteristics and uses for each REE. However, the global mining industry often uses a slightly different classification, where HREE includes Gd, Eu, Sm and Pm. Despite having a relatively low molecular weight, Y is usually classified as HREE, and Sc is not formally classified as LREE or HREE but is often considered together with REE as a whole (2).

REEs are widely used in high technology applications such as permanent magnets, electronic devices, fluid catalysts, glass industry, medical devices, military defence systems and clean energy (3). Clean technology is expected to grow significantly in the coming decades, therefore there will be a high demand for REE in the future that will lead to a higher request for global production of REE (4). Concern related to the sensitive methods for rare earth elements (REEs) determination has gradually increased over the last 10 years, which is related to the scientific and technological significance of these elements. Therefore, certainly there are current interest of development of sensitive and selective methods for determination of REEs, since the properties of these elements are very close due to the lanthanide contraction (5). X-Ray Fluorescence (XRF) has been proven over the past few decades as an efficient technique for accurate and non-destructive elemental analysis in a wide variety of environments (6). It is the method of choice for the elemental analysis of many raw materials, including REE samples. Reliability of REEs analysis results depend on analytical capability of XRF instrument's

performance and also the analyst, and were proven by its accuracy, precision and detection limits. Accuracy can be described as a measure of the closeness of the results to the true value whereas precision can be thought as a measure of the repeatability and reproducibility of an outcome. The detection limit relates to the ability of the instrument to distinguish peak intensity from fluctuations in background intensity due to count statistics, or background noise (7). In this study, analytical capability of XRF for REEs analysis in samples particularly Lanthanum (La), Cerium (Ce), Neodymium (Nd), Samarium (Sm) and Yttrium (Y) was determined by performing method validation of energy dispersive x-ray spectrometers (ED-XRF).

EXPERIMENTAL SECTION

Instrumentation and measurement condition

For this study, The XRF spectrometer used is MiniPal 4 EDXRF type (PANalytical, Netherlands), equipped with 9 W X-ray tube Rh (Max 1 mA, max 30 kV), 5 tube filters, a high resolution Silicon Drift Detector and a 12-position sample tray with sample spinner. With the spinner system, the sample rotation is constant during measurement, therefore the heterogeneity and potential errors introduced by sample preparation can be reduced (8). Measurements were done under air and helium medium. ED-XRF spectra collection, spectra installation, integration of peak areas and region of interest (ROI) and model calculations were carried out using the Minipal4 software from PANalytical. Omnian application was utilized to measure REE standard series. The application has four measurement conditions (Om1, Om2, Om3 and Om4) that had set to get the best spectrometer performance, which covered elements with low to medium Z (atomic mass) region as presented in Table 1.

Table 1. Measurement condition parameters

ED-XRF Parameters	Om1	Om2	Om3	Om4
Voltage (kV)	30	20	12	5.5
Current (μA)	300	288	430	974
Filter	Ag	Al	Al-thin	-
Atmosphere	Air	Air	He	He

Standard calibration of Rare Earth Elements

Calibration was done using standards rare earth series, which were made from CeO₂, La₂O₃, Nd₂O₃, Sm₂O₃ and Y₂O₃ (99 – 99.9% purity). The standard rare earth series were then measured using Omnian application. Calibration

curves were created by plotting the intensity vs concentration values from rare earth standards. Calibration curves were established according to the following formula:

$$y = bx + a \quad (1)$$

Where y = concentration, x = intensity produced by EDXRF measurement, b = slope and a = intercept.

Preparation of REEs Reference Material

Certified Reference Materials (CRM) In House Monazite Sand were used to validate the REEs standard curve, and were prepared by placing one and a half grams of the CRM in a disposable plastic cells that have been set up with Mylar then pressed without binder materials until the surface homogeneous. The plastic cells contains CRM were then placed in standard sample holders and loaded into the MiniPal 4 spectrometer.

Accuracy, Precision and Detection Limit

The accuracy of the method is determined by comparing the CRM In House Monazite Sand results with the certificate value. Accuracy can be expressed as% recovery. Recovery is a comparison between the measurement results and the certificate stated by the formula:

$$\%recovery = \frac{value_{analyt}}{value_{certificate}} \times 100\% \quad (2)$$

Acceptable criteria for accuracy based on the AOAC guidelines for single laboratory validation are shown in Table 2 (9). Total method precision is a combination of instrument precision and sample stability during measurement.

The precision of the method can be reported for both short-term (repeated) and long-term (reproducibility) measurements. The precision stated in %RSD, calculated from:

$$\%RSD = \frac{SD_{obs}}{Mean_{obs}} \times 100\% \quad (3)$$

Acceptable criteria for precision based on Horwitz shown in Table 3.

Table 2. Acceptable criteria for accuracy (9)

Concentration	%recovery
100%	98-101
10%	95-102
1%	92-105
0.1%	90-108
0.01%	85-110
10 ppm	80-115
1 ppm	75-120
10 ppb	70-125

Table 3. Acceptable precision criteria (9)

Concentration	%RSD (Horwitz)
100%	2
10%	2.8
1%	4
0.1%	5.7
100 ppm	8
10 ppm	11.3
1 ppm	16
100 ppb	22.6
10 ppb	32
1 ppb	45.3

The calculation of lower Limit Detection (LLD) is shown in the equation below (10):

$$LLD = \frac{3}{s} \sqrt{\frac{r_b}{t_b}} \quad (4)$$

Where:

rb = background countrate (cps)

s = sensitivity (cps/ppm)

tb = counting time background (s)

RESULTS AND DISCUSSION

In this study, five rare earth elements La, Ce, Nd, Sm and Y in the CRM In House Monazite Sand was determined using EDXRF method. The five rare earth elements are widely used in industry. In addition, these five elements are rare earth elements that are extensively analyzed in the PSTNT laboratory, and have been validated properly. Lanthanum is one of the rare earth elements that has a function to make carbon arc lights that are usually used in the motion picture industry for studio lighting and projector lights. Cerium as an alloying agent to make special metals and as a catalyst to refine petroleum. Neodymium forms approximately 18% of Misch metal, material used to make flint for matches. Several types of glass containing neodymium are utilized by astronomers to calibrate spectrometers and other types of the glass are utilized to create artificial rubies for lasers.

Samarium for example forms compounds with cobalt (SmCo₅) which are strong permanent magnets with the highest resistance to demagnetization of any known material. Although yttrium metal is not widely used, some of its compounds are used such as Yttrium oxide (Y₂O₃) and yttrium orthovanadate (YVO₄) both of which combine with europium to produce the red phosphorus used in color television (11). These elements classified as light - heavy elements, and each element has characteristic X-Ray energies, as presented in Table 4. The XRF spectrum of CRM In House Monazite Sand are shown in Figure 1. Because XRF affects the inner shell and does not bind electrons, the XRF spectrum of an element is independent of its chemical form.

The rare earth elements observed in this study have atomic number from 39 to 60, which can classified into middle and high Z elements. The number of Z impact the generating of X-rays spectrum. Table 4 shows that Ce, Nd and Sm classified as high, whereas La and Y classified as middle Z elements. High Z elements give only L lines, because K peaks from these elements are too high in energy (these electrons have high binding energies and cannot be removed with the limited voltage available in field portable analyzers). Whereas low Z elements give only K lines because L peaks from these elements are too low in energy (these photons are not transmitted through air and not detected with conventional Si-based detectors) (12). Middle Z elements may give both K and L lines.

Standard calibration

One of the fundamental methods of quantitative analysis by XRF is to create a standard calibration curve. This method involves several samples measurement with known concentrations of the element, and finding a correlation between the X-ray fluorescent intensity of the measured elements and its concentration. With reference to this relationship, the unknown concentration of the sample element is obtained only with its fluorescent X-ray intensity information (8). Table 5 presents standard calibration results for the REEs: La, Ce, Nd, Sm and Y. There is a good relationship between the expected concentration and the count rate, with a value of R² > 0.99.

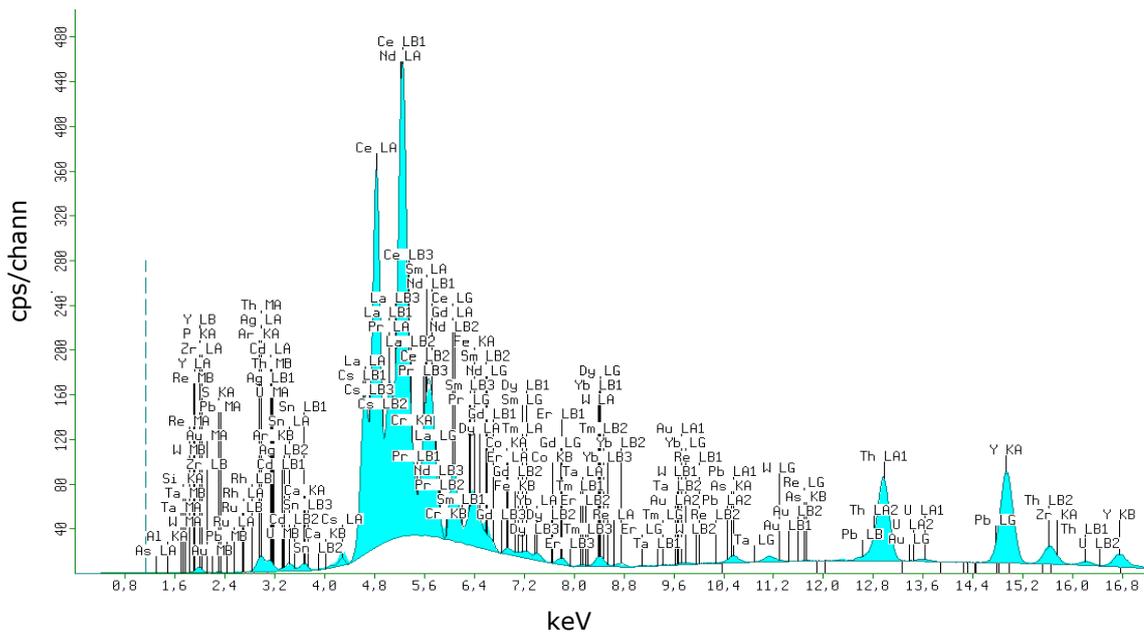


Figure 1. ED-XRF Spectrum of CRM In House Monazite Sand

Table 4. Atomic number and X-Ray Energy Characteristics

REEs	Atomic number	Classification	Kα(13) (keV)	Kβ (keV)	Lα(13) (keV)	Lβ (keV)
La	57	LREE	33.442	37.71	4.647	5.04
Ce	58	LREE			4.839	5.26
Nd	60	LREE			5.228	5.72
Sm	62	HREE			5.633	6.20
Y	39	LREE	14.958	16.74	1.924	

Table 5. Concentration range of REEs for standard calibration curve

REEs	Conc. Range (%)	Corr. (R ²)
La	0-84.42	0.996
Ce	0-81.33	0.998
Nd	0-8.57	0.996
Sm	0-68.99	0.999
Y	0-23.60	0.993

Table 6. Accuracy of REEs

Element	Measured (%)	Certificate (%)	Rec (%)
La	10.78	11.23	95.99
Ce	26.44	25.65	103.10
Nd	9.59	9.45	101.47
Sm	1.72	1.69	101.91
Y	3.14	3.10	101.57

Accuracy

Accuracy was determined by comparing the results of the CRM In House Monazite Sand. The %recovery of selected elements in the CRM is shown in Table 6. The yield of the rare earth elements corresponds well to the certified value, with recovery 95.99 to 103.10%. The recovery value above 100% is influenced by the combined uncertainty of the analysis process, from preparation to measurement. The value still in acceptable range accuracy, based on AOAC criteria.

Analytical precision

Precision was determined for repeated and reproducibility measurements. The method precision total is a combination of sample stability and the precision of instrument throughout the measurement. Precision stated in %RSD. The repeated and reproducibility of the data for several rare earth elements are presented in Table 7. Precision measurement generally provides good results based on %RSD acceptance criteria.

Table 7. Analytical precision

Element	%RSD
La	5.19
Ce	0.59
Nd	1.10
Sm	2.46
Y	1.59

Detection limits

One of the important measure for an instrument performance is detection limits or LLD (lowest limit detection). The LLD values vary corresponding to sample matrix composition and time of measurement. Increasing time of counting could give decreasing value of LLD (10). The Lower Limit of Detection (LLD) is given as a rough estimate, equal to three times the standard counting error of background intensity, as stated in the equation (4). The detection limits for the observed rare earth elements are presented in Table 8.

Table 8. Detection limits (LLD) of REEs

Element	LLD (ppm)
La	63.3
Ce	40.6
Nd	32.8
Sm	67.4
Y	8.78

CONCLUSION

Analytical capability assessment of EDXRF has been carried out by performing validation such as accuracy and precision test. The results of the several rare earth elements in this study were in accordance with the certified value, with a range of% recovery from 95.99 to 103.10%. This value of %recovery is fulfilling the acceptable criteria for accuracy. Precision was determined for repeated measurements. The precision stated in %relative standard deviation (%RSD). The %RSD values ranging from 0.59 to 5.19%, which also fulfilling the acceptable criteria. The detection limits (LLD) of ED-XRF ranged from 8.78 to 67.4 ppm. The results of this study indicate that the EDXRF spectrometer has good analytical capabilities for the analysis of rare earth elements.

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