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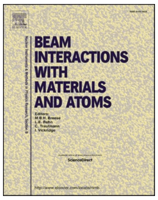

Rare-earth element comparative analysis in chosen geological samples using nuclear-related analytical techniques

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ABSTRACT

In this study, four analytical techniques for the detection of Sc, La, Ce, Nd, Sm, Eu, Tb and Lu in volcanic rock specimens from Ghana have been compared. These rock samples were examined using inductively coupled plasma mass spectrometry, X-ray fluorescence spectrometry, and instrumental neutron activation analysis. The Am-241 excitation-based X-ray fluorescence accuracies were good for Y, La, Ce, Nd, Eu, and the results were comparable to inductively coupled plasma mass spectrometry and instrumental neutron activation analysis except Silver-anode X-ray tube X-ray fluorescence. This demonstrates the limitations of the tube-based X-ray fluorescence excitation system for rare earth elements analysis, primarily caused by interference between the K-series X-ray emission from the transition metals and the relatively low intensities of L-series lines of the rare earth elements. Data on the precision and accuracy of these methods were based on IAEA SOIL-7 reference material.

1. Introduction

Rare earth elements (REEs) are acknowledged as strategic and vital minerals [1]. Therefore, many stakeholders are particularly interested in the readily available techniques to identify and quantify REEs. The need for a cost-effective method of extracting metals of economic relevance, such as REEs, is one of the primary drivers of research and development in every country. REEs have remarkably comparable physical and chemical characteristics [1]. Because traditional chemical methods for determining REEs are selective for a single element, they take a long time to complete and are not cost-effective for several samples of different elements [2]. The separation of REE using labour-intensive processes like precipitation, solvent extraction, and ion exchange before analysis by techniques like X-ray fluorescence (XRF) and inductively coupled plasma optical emission spectrometry (ICP-OES) made determining the presence of REE in geological samples challenging and expensive before the development of inductively coupled plasma mass spectrometry (ICP-MS) [3,4]. Due to its extremely low detection limits, high sample throughput, the requirement for very tiny quantities, element flexibility (major, minor, trace, and ultra-trace), and isotopic detection capacity, ICP-MS is an excellent analytical technique for the investigation of a variety of materials [1,4]. ICP-MS has been utilised by numerous researchers from across the world over the past three decades to find REE in a variety of materials [5–9]. In contrast to other regularly used analytical techniques like instrumental neutron activation analysis (INAA) and XRF, ICP-MS technology is currently employed rather extensively for the exact determination of REE in various types of materials [1,10]. The primary limitations of the XRF technique, which prevent its use for REE purposes are their lower precision and accuracy compared to other spectroscopic methods and their insufficient sensitivity for a few key components [11,12]. However, the Am-241 excitation-based system-based advance in XRF equipment recently has increased the instrument's sensitivity, allowing for improvements in both accuracy and productivity [13]. Because of this, XRF has become an alternate analytical technique for quantification of REEs.

Volcanic rock samples from Buem Structural Unit in the Dahomeyide orogenic area of south-eastern Ghana were examined using XRF and INAA, and the results were compared with ICP-MS results on the same samples at the Analytical Laboratory System laboratory in Vancouver, Canada. ICP-MS has not been widely used in Ghana due to its high cost

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Table 1
Standards produced by Fluka Chemika with their respective concentrations for sensitivity calibration.

Compound	Element	Concentration (%)	Concentration oF Other Elements (%)
$CaCO_3$	Ca	39.643	C = 11.880, O = 47.476
$CoCO_3$	Co	49.301	C = 10.048, O = 40.152
$NiCO_3$	Ni	49.396	C = 10.108, O = 40.394
ZnO	Zn	79.536	O = 19.463
AS_2O_3	As	75.588	O = 24.212
Cr_2O_3	Cr	68.414	O = 31.576
$FeCO_3$	Fe	47.720	C = 10.263, O = 41.015
$MnCO_3$	Mn	47.316	C = 10.344, O = 41.338
MoO_3	Mo	66.654	O = 33.346
$Sr(NO_3)_2$	Sr	40.988	N = 13.104O = 44.906
$CuCO_3$	Cu	50.919	C = 9.624, O = 38.460
KBr	Br	66.474	K = 32.523
$KHCO_3$	K	38.663	H = 0.100, C = 11.877, O = 47.462
–	S	32.06	–
–	Ti	47.8	–
$NaCl$	Cl	60.059	Na = 38.946
$AgNO_3$	Ag	63.373	N = 8.229, O = 28.199
BaO	Ba	87.772	O = 10.226
$CsNO_3$	Cs	66.142	N = 6.971, O = 23.886
CdO	Cd	87.540	O = 12.460
$HgCl_2$	Hg	73.138	Cl = 25.853
HIO_3	I	71.781	H = 0.57, O = 27.149
PbO	Pb	91.903	O = 7.096
–	Sn	99.00	–
WO_3	W	79.297	O = 20.703

and accessibility. INAA has been used by several studies to find REE in a variety of earth and environmental materials at very low quantities [14–20]. To better understand the geochemical behaviour of beach sands from Tamil Nadu, India, Ravisankar et al. (2006) used INAA to measure REE [21]. Two XRF methods were investigated: the first used an Am-241 excitation-based system to excite the sample K-series and the second used an Ag-target tube to excite the sample L-series.

2. Materials and methods

2.1. Samples

The rock samples DK4, DK6, and DK9 used in this work have been previously analysed by the ICP-MS method [22]. These samples were collected from the Pan-African Dahomeyide belt in southeast Ghana's Buem Structural Unit, primarily from the Asukawkaw, Bowiri-Odumase, and Nkonya localities. The reference material (IAEA-Soil 7) is produced by International Atomic Energy Agency and the chemical standards are produced by Fluka Chemika (See Table 1).

2.2. Instrumental neutron activation analysis

DK4, DK6, DK9, and SOIL 7 samples, were pulverized into a homogeneous powder and 150 mg of each was weighed, wrapped in a thin polyethylene sheet, and heat-sealed. IAEA soil 7 reference material sample and REE-containing materials were exposed to thermal neutron flux of $5.0 \times 10^{11} n/cm^2 s^1$ using the Ghana Research Reactor-1 (GHARR-1) with an output of 17 kW. Based on the half-lives of the relevant components, three types of irradiation procedures were adopted: Nuclide half-lives that are short (between 1 min and t (1/2) 2.5 h), medium (between 12 h and t (1/2) 3 days), and long (t (1/2) > 3 days) are the three categories [23].

2.3. X-ray fluorescence

XRF is a non-destructive analytical technique used to determine a material's elemental composition. XRF analyzers can detect a sample's chemistry by measuring the fluorescence (or secondary) X-ray that a sample emits after being excited by a primary X-ray.

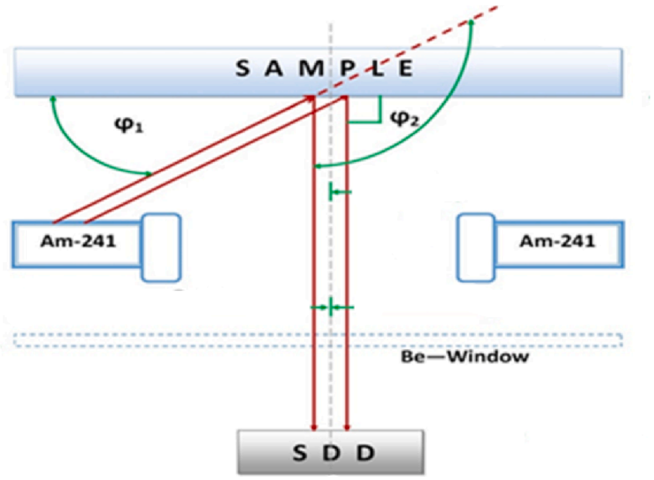

Fig. 1. The ideal source-sample-detector geometry for the Am-241 excitation-based system (measurements in degrees and milliliters).

2.3.1. X-ray fluorescence equipment

X-Ray Spectrometer Re-configuration: The benchtop XRF spectrometer at GAEC was attached to a developed Am-241 excitation-based system. The design and the construction of the excitation system focus on three main parts, namely:

(i) An excitation source.
(ii) A sample
(iii) A detection system

2.4. Am-241 excitation-based system irradiation and Measurement

The prepared pellets were exposed to radiation using an Am-241 excitation-based source (100 mCi).

Sensitivity, 25 oxide standards were used for measurements, which were used to create calibration curves. The IAEA-Soil 7′s elemental concentration was established. The element's content of the IAEA-Soil 7 reference sample is displayed in Table 3. Results for the reference material are represented here as the mean values of three measurements, with standard deviation (SD). The recommended values and measured values agree well, and the errors are often between 5% and 10%.

An X-123 Silicon Drift Detector (Amptek Technologies) with a thickness of 500 μ and a resolution of 125 eV full width at half maximum resolution at 5.9 keV (55Fe) at 11.2 microseconds peaking time had been installed on the Am-241 excitation-based source. The K-shell characteristic X-ray was excited for 3000 s using an Am-241 excitation-based source. At incident angle (φ_1) of 50.5^0 and a take-off angle (φ_2) of 90^0 as shown in Fig. 1. Sample-detector separation was measured at 28.6 mm. The QXAS programme [24] was used to process the X-ray fluorescence data, and the net peak intensities of the K-series lines were determined by fitting the spectra with the AXIL. The AXIL was used to calculate the elemental concentration. The concentration values are the three measurements' averages.

2.4.1. Sample preparation for X-ray fluorescence

Standards: IAEA-Soil 7 reference material and chemical standards were powdered, and 10 g of each was pressed at 15 tonnes of pressure to produce thick pellets measuring 2 cm in diameter. Before being exposed to radiation, the pellets produced were desiccated for 24 h.

Rock samples: The rock samples were broken up, pulverised, and put through a sieve with a mesh size of 100 μm. At the Ghana Atomic Energy Commission (GAEC), pellets were produced utilising a hydraulic pelletizer (Carver Technologies, Auto-CrushIR, Wisconsin, US) and a

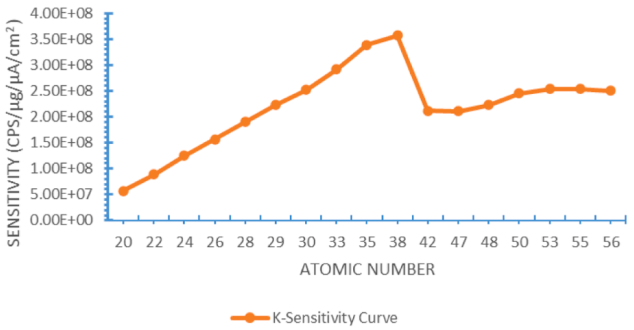

Fig. 2. Am-241 Kα-Sensitivity Curve.

stainless-steel pellet die with a 2.5 cm diameter. A pellet is created by compressing sample powders at a rate of 20 tonnes per square inch between two flat, polished discs. Each sample was divided into pellets having a diameter of 2.5 cm and a thickness of 0.5 cm, each weighing 10 g. The pellets were kept overnight in the 150 mm desiccator (AS ONE, 240, Vietnam) before being analysed by the XRF. The pellets were exposed to radiation using an Ag-anode X-ray tube and Am-241 excitation-based XRF system. Using a silicon drift detector, the distinctive L-series X-rays of Cerium (Ce) and Europium (Eu) were measured with Ag-anode X-ray tube. The 120 s irradiation period used a current of 5 µA and a voltage of 45 keV. These systems' calibration peaks were K-K, Br-K, and Mo-K. IAEA-AXIL evaluated the net intensities of the distinct characteristic X-rays based on non-linear least-squares fitting and the Elemental Sensitivity method. The concentration values are the three measurements' averages.

2.4.2. Quantification method for XRF

For a quantitative X-ray fluorescence (XRF) analysis, it is necessary to convert the recorded intensities of the characteristic radiation to the concentrations of the components to be evaluated (analytes). This approach is based on the relationship between the intensity of the excitation source, the concentration of the analyte, the overall composition of the sample, and the absorption properties of the sample.

$$I_i(E) = \frac{S_i(E).C_i}{a(E)}$$

$S_i(E)$ is the sensitivity of the element in counts/ppm/second, $I_i(E)$ is the fluorescent intensity of the element in counts/seconds, C_i is the concentration of the element i in the element in ppm and a(E) is the average absorption correction factor.

3. Result and discussion

3.1. Calibration

For XRF analysis, calibration is the relationship between the atomic number of the element of interest and the number of x-rays emitted mg/kg of the element of interest per second [25,26]. The levels of REEs found in various samples were determined by comparing them to calibration curves made from the oxides of twenty-five standard samples (S, Cl, K, Ca, Ti Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Sr, Mo, Ag, Cd, Sn, I, Cs, Ba, W, Hg, and Pb). The average peak areas obtained from the irradiation of five 100 g standard pellets prepared in the same manner as the sample pellets were used to construct the concentration calibration curves. A Fig. 2 and Fig. 3 shows a typical calibration curve made from the standards for a 6000-second exposure to a 100 mCi Am-241 excitation-based system and Ag-anode tube XRF exposure of 120 s respectively. The calibration curves are used to determine an element's concentration in (mg/kg) in given sample is express as:

$$C_i = \frac{I_i(E)a(E)}{S_i}$$

Table 2
A detection limit of REEs using Am-241 excitation-based XRF, INAA and ICP-MS in mg/kg.

Element	Am-241 Source	INAA	ICP-MS
La	2.00	0.19	0.06
Ce	2.00	0.03	0.05
Nd	2.00	3.03	0.10
Sm	2.00	0.08	0.04
Eu	5.00	"n/c"	0.02
Gd	5.00	"n/c"	0.04
Tb	"n/c"	0.10	0.01
Er	2.00	"n/c"	0.03
Yb	"n/c"	0.08	0.01
Lu	"n/c"	0.04	0.01
Y	0.01	0.01	0.30
Sc	0.1	0.01	4.00

Note: "n/c" - value was not calculated. ICP-MS [22].

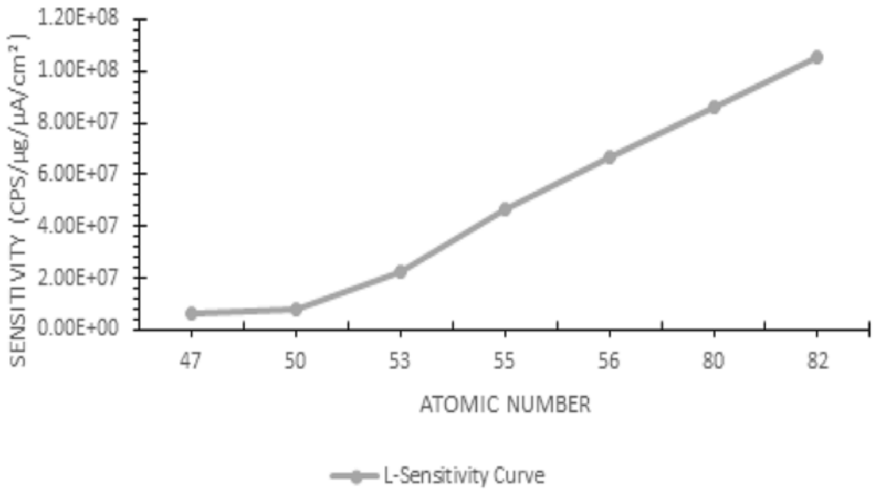

Fig. 3. Ag-anode X-ray Tube Lα-sensitivity curve.

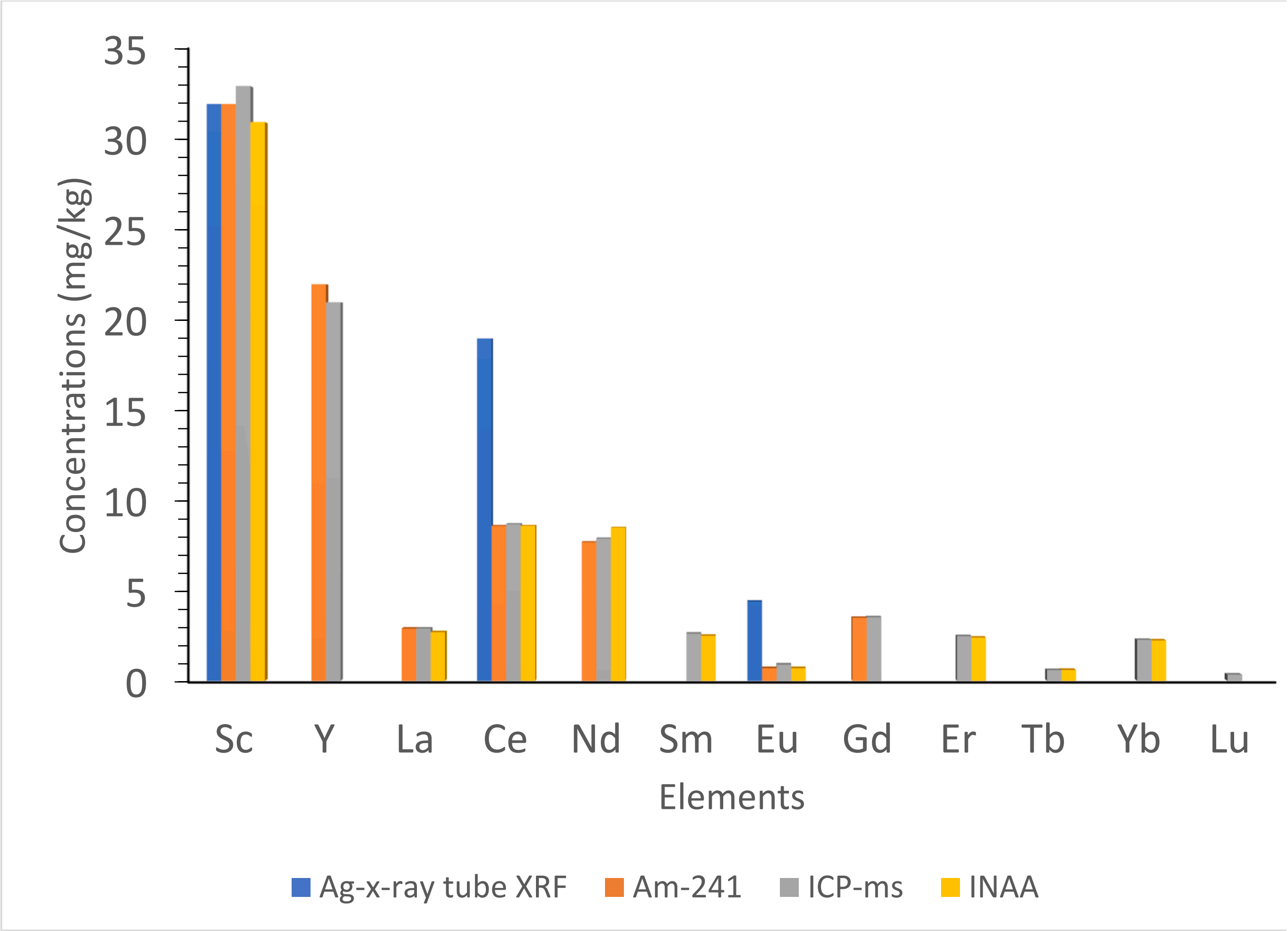

Fig. 4. Graph displaying the REE concentrations in sample DK4.

3.2. Detection limit

The detection limit obtained (Table 2) are comparable to the previous studies. ICP-MS [27] INAA [28] XRF [29] Am-241 excitation-based XRF [21].

3.3. Matrix effect

The standard reference materials are chosen for the proper application of the XRF method so that they match the matrix type and concentration of the target measurables, the rock samples were examined in a powdered form. The reference material available that is closers in a matrix to the sample analysed is IAEA-Soil 7 and furthermore, it contains some REE to validate the method. The use of the IAEA-Soil 7 reference material for REE analysis in rock samples in this study is justified by the fact that both the samples and the standards have a geological matrix that is predominately composed of light and heavy elements, making them suitable for use in this study.

Experimental research on this assumption was conducted [31]; it was found that the systematic divergence in the calibration due to various matrices were estimated to be less than 10% for majority of the components.

Replicate irradiations were used to test the sample homogeneity, and it was discovered to be within 5%. The discussions mentioned above support the calibrating techniques applied in this investigation.

A comparison of the outcomes for the Ag anode X-ray Tube spectrometer, the attached Am-241 excitation-based system, INAA, and ICP-MS is shown in Figs. 4-6. There is still some variance in the concentration levels despite the Ag anode X-ray tube spectrometer spectra lines' acceptable match. In samples DK4, DK6, and DK9, as well as Er in samples DK4 and DK8, it was unable to detect Y, Nd, Gd, Tb, Yb, and Lu. The Y, Nd, and Gd in DK4, DK6, and DK9 could all be detected and quantified by the associated Am-241 excitation-based system, as well as

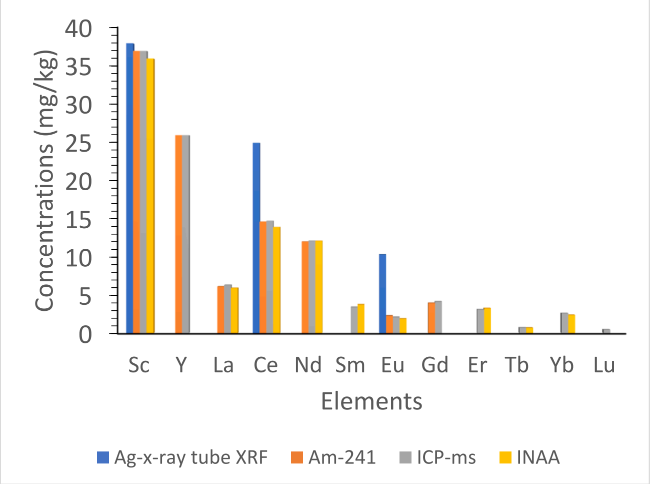

Fig. 5. Graph displaying the REE concentrations in sample DK6.

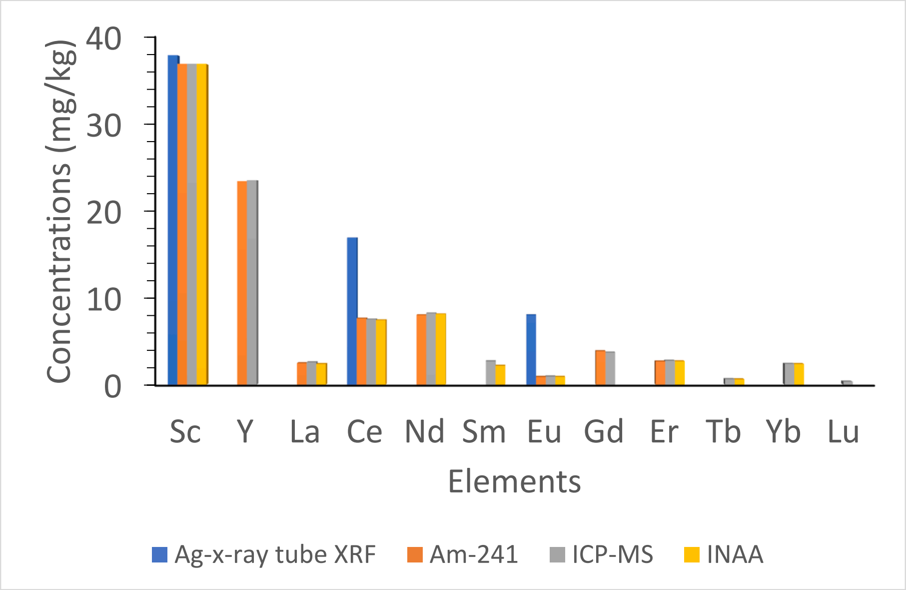

Fig. 6. Is a graph that displays the ree levels in sample dk9.

Table 3
Comparative concentrations (mg/kg) of REE in IAEA-Soil 7 by INAA, ICP-MS, Ag-Tube XRF and Am-241 XRF.

Elements	Soil 7 (REEs Elements) Expected value (mg/kg)	Ag-Tube XRF measurements			Am-241 XRF Measurement			INAA Measurements		
		Observed value (mg/kg)	Recovery (%)	SD	Observed value (mg/kg)	Recovery (%)	SD	Observed value (mg/kg)	Recovery (%)	SD
Sc	8.3±5.2	7.0±7.2	**84.3**	5.2	8.1 ± 2.5	**98.0**	2.5	8.1 ±1.3	**97.6**	1.3
La	28.0±1	“n/d”	“n/c”	“n/c”	27.5±3.8	**98.2**	3.8	27.2±1.1	**97 .0**	1.1
Ce	61.0±6.5	“n/d”	“n/c”	“n/c”	60.5 ±2.5	**99.2**	2.5	60.4±2.3	**99.0**	2.3
Nd	30.0±6	“n/d”	“n/c”	“n/c”	29.4 ±3.0	**98.0**	3.0	29.7±1.2	**99.0**	1.2
Sm	5.1±0.35	n/d“	“n/c”	“n/c”	4.6±2.0	**90.2**	2.0	4.3 ±0.25	**84.3**	0.25
Eu	1.0±0.2	1.2± 0.8	**120.0**	3.8	0.8 ±0.4	**80.0**	2.7	0.8±0.05	**80.0**	0.05
Tb	0.6±0.2	“n/d”	“n/c”	“n/c”	“n/d”	“n/c”	“n/c”	0.4 ±0.03	**66.7**	0.03
Yb	2.4±0.35	5.1 ±3.4	**212.0**	13.4	“n/d”	“n/c”	“n/c”	2.3±0.09	**95.8**	0.09
Lu	0.3±0.1	“n/d”	“n/c”	“n/d”	“n/d”	“n/c”	“n/c”	0.3 ±1.3	**100**	1.3

“n/c” - value was not calculated.
“n/d” - element was not determined.
Recovery is calculated as (Observed Value / (Expected Value) × 100%.

Er in DK4, which EXP-1 was unable to do.

However, the current REEs findings utilising INAA and ICP-MS show that the outcomes were comparable to those reported in other works [1,9,16,18]. With a few exceptions, the current Am-241 excitation-based system is the most effective one (see Table 3). This method is effective for REEs within the sensitivity calibration curve’s range.

3.4. *Evaluation of Am-241 EDXRF, Ag-Tube EDXRF, INAA, and ICP-MS results*

The connected Am-241 excited-based system was compared to the concentration values of the various methods, including the Ag anode-X-ray tube spectrometer, INAA, and ICP-MS, that were employed for this study’s validation. The concentration values of Am-241 excitation-based system (2.9, 7.1,14.1,55.1,91.6, 107) mg/kg was plotted against that of the instrumental neutron activation analysis (3.1, 5.9,25.5,16.3,210.0,206.0) The linear regression method and the correlation analysis method were both used (see Figs. 7-9). Multivariate regression robust statistics and equations were used to statistically analyse the performance of the attached Am-241 excitation-based system [30]. For every analyte’s the.

Excited-based system Am-241 = B [INAA (mg/kg)] + A,

when the slope (B) and intercept (A) were computed. B = 1 and A = 0. The intercept (A) should be close to zero (0) and the slope (B) should be close to 1 as illustrated in Fig. 7 if the connected Am-241 excited-based system concentrations and the INAA concentrations of elements are consistent for REEs. As a result, there was no discernible difference between the two methodologies’ results for REEs. On the other hand, under identical circumstances, statistically significant differences in the estimated element concentrations of REEs using the Ag anode X-ray tube spectrometer were found. When the concentration values of Am-241 excitation-based system (9.4,0.3,27.2) mg/kg was plotted against that

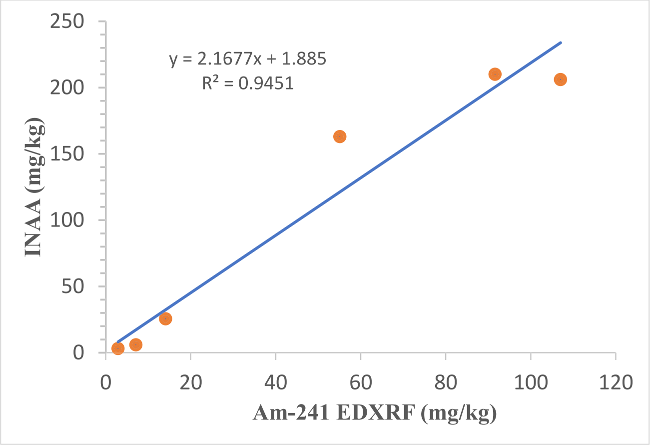

Fig. 7. The graph compares the outcomes for REEs from INAA and Am-241excitation-based EDXRF, together with the correlation and R^2 values.

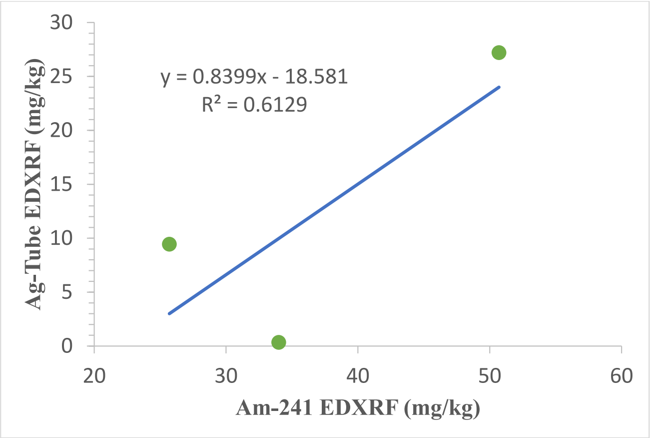

Fig. 8. The graph compares the REEs results from the Ag anode X-tube spectrometer and Am-241 excitation-based system to the correlation equation and the R^2 value of 0.6129.

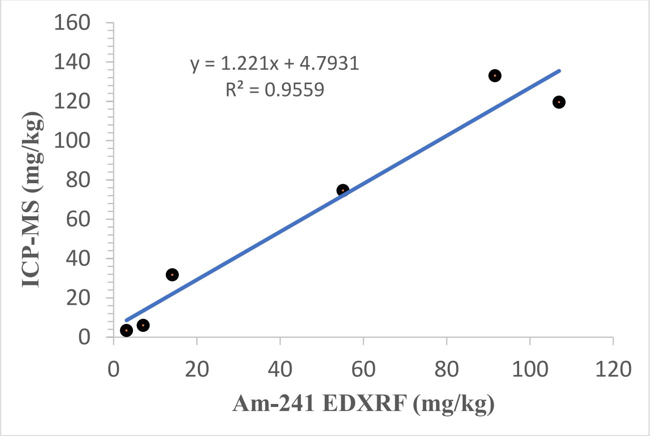

Fig. 9. The graph compares the REEs in sample DK6 as determined by ICP-MS and the associated Am-241excitation-based EDXRF system, as well as the correlation equation and R^2 values.

of Ag-tube XRF (25.7, 34.0,50.7). The validation curves for REEs had slopes that were almost one (0.8399), but their intercepts (-18.581) were not nearly zero (0), as shown in Fig. 8. The standard deviation (3.8–13.4) of discrepancies for the Ag anode X-tube spectrometer was also very high and significantly different from zero.

This demonstrates the limitations of the tube-based XRF excitation system for REE analysis, primarily caused by interference between the K-series X-ray from the transition metals and the relatively small intensities of L-series X-ray of the REE. As a result, concentration values are less accurate and the range of REE that can be analysed is constrained.

The concentration values of Am-241 excitation-based system (3.1, 7.1, 14.1, 55.1, 91.6, 107.0) mg/kg was plotted against that of the inductively coupled -mass spectrometer (3.4, 6.0, 31.7, 74.6, 133.0, 119.5) as shown in Fig. 9. In Fig. 9 and Fig. 7, the slope, intercept, and linear correlation coefficient (R^2) values of the attached Am-241 excitation-based system, INAA, and ICP-MS were all close to 1, close to zero (0), and higher than 0.95 in all cases. These findings demonstrated a perfect agreement between the techniques used by the attached Am-241 excitation-based system, INAA, and ICP-MS. However, the current REEs findings utilising INAA and ICP-MS show that the outcomes were equivalent to those reported in other works [1].

As seen in Table 3, the standard deviation (SD) values for this study's elemental sensitivity method for the Ag-anode X-Tube spectrometer ranged from 8.9 to 10.0 mg/kg and from 2.0 to 3.8 mg/kg for the attached Am-241 excitation-based system. The INAA standard deviation values ranged from 0.09 to 2.3 mg/kg. When the required X-ray fluorescence spectrometers' SD is less than 10% and, occasionally, when elements of a certain concentration are constrained, the SD values are low [31,32]. The findings demonstrate that the elemental sensitivity method for the attached Am-241 excitation-based system is an accurate and comparable method for the determination of REEs.

4. Conclusions

The Am-241 excitation-based system was proved to be a trustworthy, accurate alternative for REEs analysis through comparison analysis results with ICP-MS and INAA techniques. Since sample preparation is minimal and analysis time is shorter than with other techniques, the Am-241 excitation-based system provides opportunities for quick and accurate routine analysis of a large number of samples.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

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