

Characterisation, quantification and recovery of rare earth elements in South African coal fly ash samples

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Rare earth elements (REEs) are naturally distributed throughout the Earth's crust, typically in low concentrations. They are not typically found in isolation but rather present in various minerals, often in amounts too minute for cost-effective extraction. Fly ash is among the sources that are deemed economically viable for extracting REEs. This paper aims to create environmentally sustainable approaches for measuring and reclaiming REEs in coal fly ash samples. The study involved characterisation and quantification of fly ash samples collected from various coal power stations, digested using microwave acids digestion and advanced analytical techniques including X-ray fluorescence (XRF), X-ray diffraction (XRD), inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES). The XRF only shows the presence of REEs from all three fly ash samples with a range of 40 to 100 ppm and mineral oxide ranging from 0.1 to 50 %. The XRD results show that fly ash sample is a siliceous-rich sample with abundant minerals such as quartz (SiO₂), magnetite (Fe₃O₄), and mullite (Al_{4.52}Si_{1.48}O_{9.74}). The recovery percentage (%) from ICP-MS showed an excellent percentage yield (80 - 120%) compared to the ICP-OES instrument (50 - 120%) for REEs. The ICP-MS data indicate that all fly ash samples have a high concentration of light rare earth elements (LREEs) and a lower concentration of heavy REEs (HREEs). Excellent recovery was obtained by ICP-MS in a developed microwave acid digestion method. The concentration of REEs obtained from ICP - MS and OES in fly ash samples ranged from 50 ppm to 200 ppm for LREEs and 0.5 ppm to 20 ppm for HREEs.

Keywords: REEs, fly ash, microwave-acid digestion, LREEs, HREEs, XRF, ICP-MS/OES

INTRODUCTION

Rare earth elements (REEs) are elements that exist in the Earth's crust and are found in low concentrations. These elements are mostly separated into the different minerals in which they exist; in most cases, their concentration is too small for economical extraction. REEs are the 15 lanthanide series elements (elements 57-71) as well as scandium (21) and yttrium (39) (Eterigho *et al.*, 2021). REEs are used in different industrial processes; these elements are considered important elements in terms of the production of green technology and electronic appliances, and they are also used in the medical and defence industries (Scott *et al.* 2015). They have been recognised as being important in research and development for several scientific and commercial applications. Coal and coal by-products such as ash and other waste materials have been found to contain REEs in varying amounts and concentrations. The demand pick for REEs in the current market is higher than the supply pick, which is growing steadily as well. As the world shifts towards being carbon footprint-free, the production of green clean energy and technology is expected to guide the demand for REEs (MINERAL 2010). REE consumption is anticipated to be guided by the demand for green technology, such as wind turbines and other technology production that uses permanent magnetic products.

Since REEs are isolated according to their characteristics, their supply and demand chains vary, and the levels at which they are found differ according to their mining sites. The South African economy holds a bright and promising future regarding REE production. This is because the South African economy depends largely on the coal mining industry to generate energy (January 2017).

REEs can be grouped into different groups due to their abundance and chemical properties. Elements with lower atomic mass numbers (57 – 62) from samarium to lanthanum are grouped as light rare earth elements (LREEs), while elements with atomic numbers (63 – 71) from europium to lutetium are referred to as heavy rare earth elements (HREEs). REEs are found in numerous minerals, but the main sources of these elements are primarily limited to three minerals: bastnaesite, monazite, and xenotime. These minerals contain higher concentrations of REEs compared to others, making them the primary targets for REE extraction (Lie and Liu 2021).

Residual fly ash is saturated with organic materials from the flue gases of furnaces at pulverised coal power plants. Burning coal in any pulverised coal boiler produces minerals that are retained from coal, and those minerals are converted into chemical species that are chemically reactive or could be chemically activated. At varying concentrations, REEs can be found in coal byproducts, including ash, coal-related sludge, and mine drainage. There is a possibility that some coal ash contains a higher percentage of heavy (generally more valuable) REEs compared to natural ores (Peterson *et al.*, 2017).

Determining REEs is extremely challenging, whether through extraction methods or instrumental techniques, due to their low concentrations and the presence of other minerals, as well as their chemical similarity. Recent research on fly ash primarily focuses on determining trace element concentrations and leaching effects using techniques such as inductively coupled plasma-optical emission spectroscopy (ICP-OES), gas chromatography-mass spectrometry (MS), X-ray fluorescence (XRF), and X-ray diffraction (XRD) as well as scanning electron microscopy (SEM) (Rajendran *et al.*, 2006). It is essential to dissolve refractory minerals (including zircon, garnet, cassiterite, tourmalines, chromite, etc.) thoroughly prior to calibrating solution-based instrumental analytical methods for geological and metallurgical materials. Traditional techniques employing high-temperature and high-pressure Parr Bombs with a mixture of strong acids like HCl, HNO₃, and HF are effective in fully dissolving samples with highly refractory phases, which is essential in the mining and metallurgical industries (Crock *et al.*, 1986). In this study, three acid combinations were employed to digest coal fly ash samples and Certified Reference Materials (CRM) samples in the microwave for analysis using both ICP-MS and ICP-OES. Press pallets were utilised for XRF analysis sample preparation. Various REE-CRMs, including CGL 111, 124, 126, and AMIS 276, were utilised to develop and optimise a method for analysing REEs in coal fly ash samples. Microwave acid-assisted digestion is a technique used in analytical chemistry for sample preparation, particularly for the recovery of REEs from various matrices such as ores, rocks, soils, sediments, or industrial products. Microwave heating allows for much faster digestion compared to conventional methods. The high-frequency electromagnetic radiation penetrates the sample, generating heat internally, which leads to rapid and uniform heating (Verma *et al.*, 2022). This significantly reduces digestion times from hours to minutes, thereby increasing sample throughput and overall laboratory efficiency. The high temperature and pressure conditions achieved in microwave digestion systems facilitate more efficient decomposition of complex matrices. This results in more complete dissolution of the sample and better recovery of analytes by ensuring reproducibility and reliability of results. The enhanced digestion efficiency improves the accuracy and precision of subsequent analytical measurements.

The goal of this investigation was to develop an ICP method that is accurate, precise, rapid, and reliable for analysing REEs in coal fly ash. The objective was to expedite the microwave acid-assisted digestion techniques for REEs analysis.

MATERIALS AND REAGENTS

Reagents, Standard Solutions, and Certified Reference Materials

Three distinct coal fly ash samples from different coal power stations (Kusile, Matla, Kendal) were gathered, each weighing approximately 5 kg to 20 kg in fine powder form. Prior to analysis, all samples underwent milling to ensure they passed 95% of 75 μm . Solutions were prepared using Millipore purified water (18 M Ω), and high-purity reagents ($\geq 99\%$) obtained from Sigma-Aldrich South Africa were utilised. A standard stock solution of 1000 ppm with multi-REEs was used to prepare a 1 ppm stock solution of REE standards; ICP grade Accu Standard was purchased from Ultra spec (de Bruyn, South Africa). The CRMs CGL111 and CGL124, obtained from the Mongolia Central Geological Laboratory, are composed of monazite and xenotime, respectively.

Sample Preparation, Preparation of calibration STD and Instrumentation

Approximately 0.2000+/-0.003 g of coal fly ash sample was weighed directly into Teflon-PFA digestion vessels, followed by the addition of 3 mL HCl, 9 mL HNO₃, and 3 mL HF. A closed vessel, microwave-heated for 40 minutes at a maximum temperature of 200 to 220°C was then used to digest the samples as illustrated in Table I. The samples were left to stand at room temperature for 15 to 30 minutes before digestion.

Table I. Optimisation condition set for Mar 6-microwave digestion

Steps	Power (W)	Ramp time (Minutes)	Temperature (°C)	Hold time (Minutes)
1	600	10	200	5
2	1000	5	220	30
3	1000	5	220	5

Calibration standards were prepared in 2% HNO₃. There was also an internal standard of 1 ppb g L⁻¹ of Re and In included in each standard. Calibration standards were diluted according to the concentration range of 1 ppb to 100 ppb for ICP-MS and 0.5 to 1000 ppm for ICP-OES. The content of REEs in the obtained solutions was measured by ICP-MS and OES (Agilent 7800 MS and 5900 OES instrument) under the instrumental conditions presented in Table II.

Table II. ICP-instrument operation conditions

Parameter	Actual Value
Plasma power	1 400 kW
Plasma gas	Argon
Plasma gas flow rate	17 L min ⁻¹
Auxiliary gas flow rate	1.4 L min ⁻¹
Nebuliser gas flow rate	0.75 L min ⁻¹

RESULTS AND DISCUSSION

X-ray Fluorescence Results

XRF analysis was conducted to identify the concentrations in the samples from the different coal power stations from the results obtained. The ash samples from the various power stations contained only LREEs in the range of 40 to 100 ppm (Table III), while in Table IV the mineral oxides ranged from 0.1 to 50%, with quartz being the major oxide. The presence of mineral oxide from all samples confirms that those ash samples are of high quality. The XRF results for REE analysis are presented in Tables III to IV. Table IV illustrates all three fly ash samples containing REEs despite their geological location. All three samples show a high content concentration of LREEs from XRF analysis, while HREEs were not detected from all different samples.

Table III. Concentration of REEs in different power stations determined by XRF

Sample ID	Kusile power station	Matla power station	Kendal power station
ELEMENTS	Concentration (ppm)		
La	104.7	65.9	97.6
Ce	191.2	138.1	185.8
Nb	33.8	37.1	39.2
Y	90.7	78.6	83
Ga	43.7	57.4	62.4

Table IV. Major oxide composition determined in fly ash samples

Sample ID	Kusile power station	Matla power station	Kendal power station
Oxides	Mass (%)		
Al ₂ O ₃	31.74	24.81	31.24
SiO ₂	58.99	62.77	52.65
Fe ₂ O ₃	4.444	4.573	3.615
CaO	7.6502	4.0312	5.8987
MgO	1.3948	0.7650	1.1457
Na ₂ O	0.3863	0.2220	0.1023
K ₂ O	1.0559	0.9815	0.7396
TiO ₂	4.0516	3.8208	3.7855
P ₂ O ₅	1.2761	0.6985	0.4467

X-ray Diffraction Results

XRD analysis was conducted to identify minerals that are present in the coal fly ash sample. The analysis showed that the sample consists predominantly of mullite with major amounts of quartz. The iron oxide magnetite is present in trace amounts (Table V). The qualitative results relate only to the crystalline components identified. Overall, the fly ash sample is silicate-rich.

Table V. Qualitative XRD results of the mineral composition in the fly ash sample

Mineral	Chemical Formula	Relative abundance
Quartz	SiO ₂	Major
Magnetite	Fe ₃ O ₄	Trace
Mullite	Al _{4.52} Si _{1.48} O _{9.74}	Predominant

ICP-MS and ICP-OES analysis

ICP-MS and ICP-OES techniques were used to determine the concentration of REEs in the fly ash samples. Before the analysis of each CRM and sample, calibration of the instruments was performed using a multirare earth element standard. This was done to ensure that the instrument was adequate to respond to the analytes of interest. The regression plot obtained for all REEs ranged from R² = 0.9997 – 1.0, as illustrated in Figure 1.

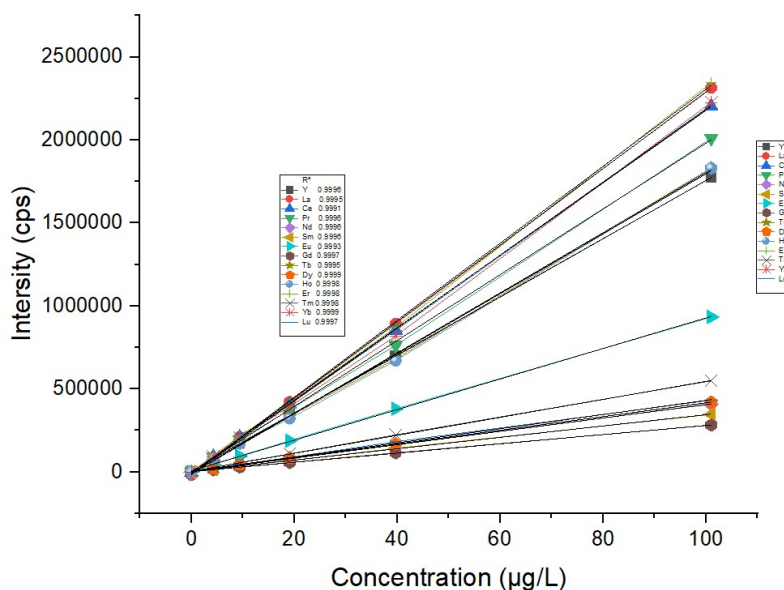


Figure 1. Regression plot for REEs at various concentration ranges.

Certified Reference Material Results for Validation

Three CRMs, CGL 111, CGL 124, and AMIS0276, of REEs were selected and used as part of validating techniques used for the determination of REE concentrations. Values of each CRM concentration obtained were compared against the certified values and calculated percentage recovery (%). The recovered results from the microwave acid digestion method (HNO₃, HCl, and HF) used for digestion in selected CRMs (CGL 111, CGL 124, and AMIS0276) were well digested. The digestion method was iterated over multiple trials (n=10) to optimise the microwave conditions and enhance the recovery of REEs in the selected CRMs. The aim was to align the results with the certified values, indicating a high

level of accuracy and precision in the analytical process (Ditri 2017). The obtained results, in conjunction with the certified values, were employed to calculate the percentage recovery (%) of REEs for all three chosen CRMs. The recovery was determined through the following calculation method:

$$\% \text{Recovery} = \frac{\text{Obtained value}}{\text{Certified value}} \times 100\% \quad [1]$$

ICP-MS and ICP-OES Results

The results of the REE concentration from all reference selected CRMs obtained from ICP-MS through microwave acid digestion methods showed good recovery, as shown in Figure 2. The optimisation shows a good response for both the microwave and ICP-MS instruments.

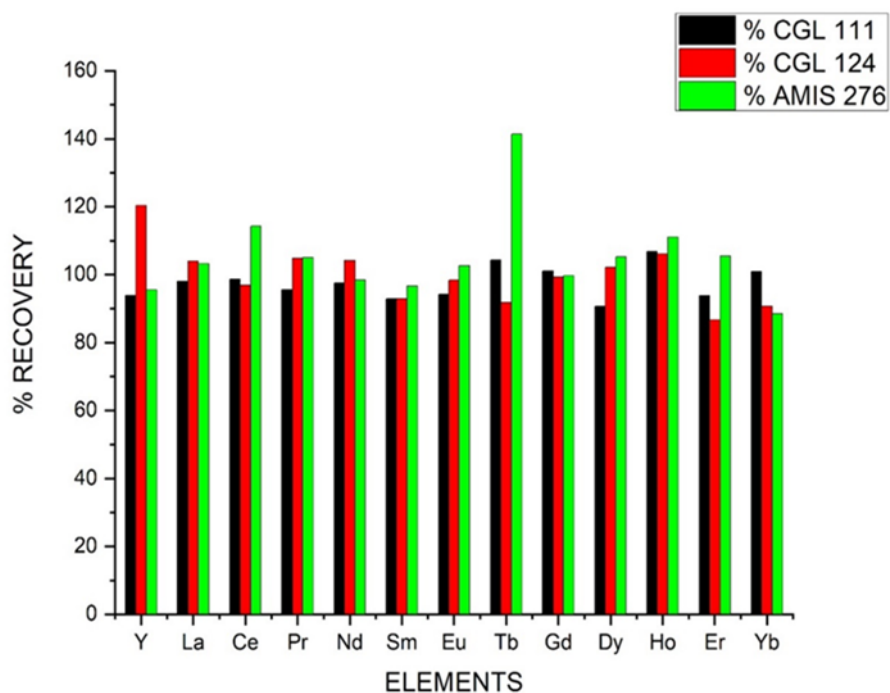


Figure 2. Recovery % comparison of the different CRM by microwave and ICP-MS.

ICP-OES shows low sensitivity in low-REE CRMs, as observed in AMIS0276. The instrument was underrecovering the CRM values due to a lack of sensitivity in the low-concentration REE sample. The instruments show a good trend and reproducibility in highly concentrated REE CRMs such as CGL 111 and CGL 124, as illustrated in Figure 3.

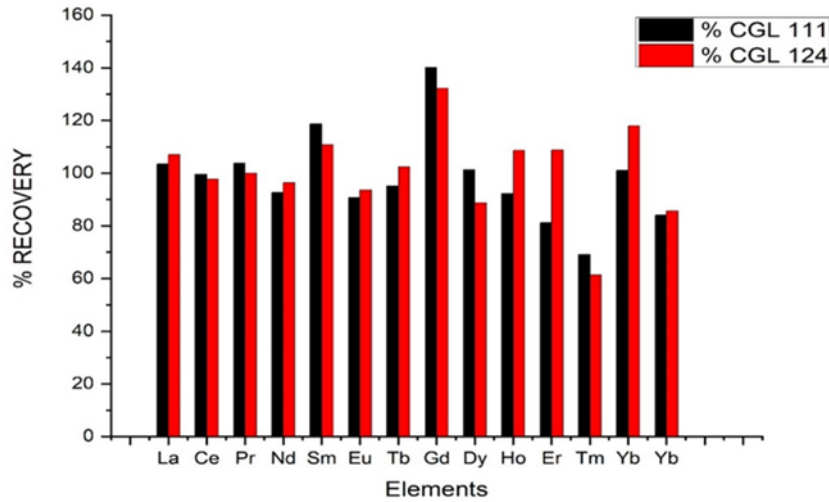


Figure 3. Recovery % of REEs from CRMs by ICP-OES.

The recovery of REEs from REE CRMs was successful. To obtain the best possible applicable digestion methods and analytical techniques for the analysis of REEs, three internationally CRMs were used (CGL 111, 124 and AMIS0276) to develop closed vessel methods that can be employed to analyse REE samples from fly ash samples. After establishing suitable parameters for the microwave digestion method, REEs were quantitatively recovered using the acid digestion method under closed vessel conditions and analysed by ICP-MS and OES instruments. ICP-MS demonstrated good recoveries (80-120%) for most major trace elements, whereas ICP-OES analysis showed recoveries of approximately (50-120%), as illustrated in Figure 4. According to the method validation exercise, criteria for the method acceptance such as selectivity, repeatability, reproducibility, linearity, and recoveries are used for method acceptance (Gray *et al.*, 2015). One of the criteria applied in this investigation was that recoveries of check solutions should be within $\pm 20\%$ of the true value.

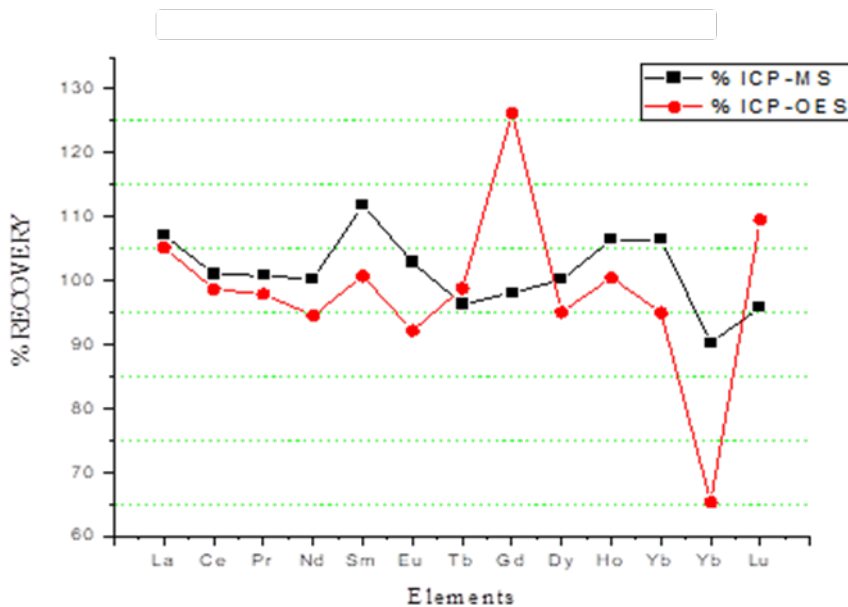


Figure 4. Comparing average % between ICP MS & OES analysis.

REE results from fly ash samples

All three acquired fly ash samples were subjected to microwave acid digestion methods to recover the REE concentration. The samples were analysed using the ICP-MS technique, as it was the technique that showed good recovery through the validation process compared to ICP-OES. From the obtained results, there is a slight difference between the concentrations of REEs in all three samples from the Kusile, Matla, and Kendal power stations. The samples showed similar concentration levels for all the elements. All three samples showed a high concentration level of LREEs (Y, La, Ce, and Nd) ranging between ~50 ppm to ~200 ppm, whereas the HREE (Sm, Eu, Tb, Gd, Dy, Ho, Er, and Yb) concentration was lower throughout all samples, ranging between ~0.5 ppm to ~20 ppm, as illustrated in Figure 5.

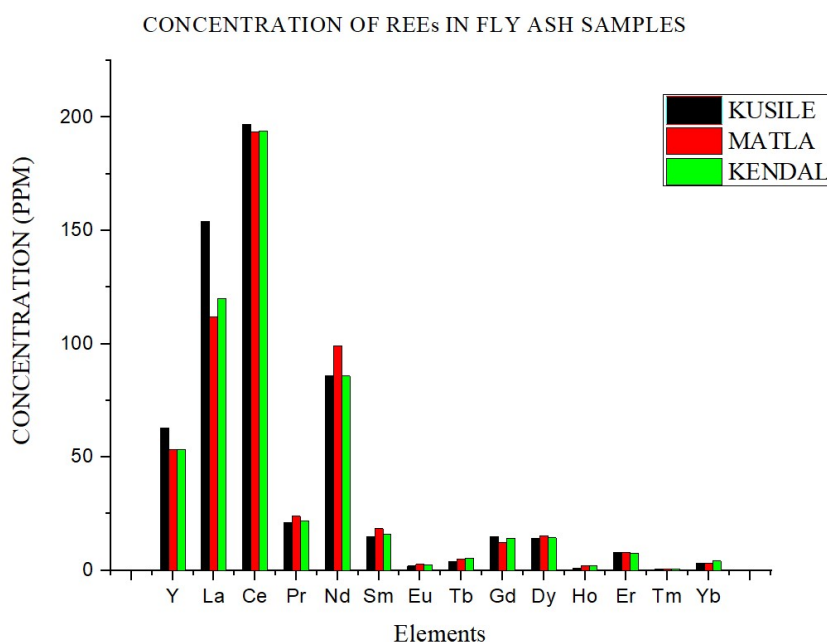


Figure 5. Recovered concentrations of REE in various samples by ICP-MS.

CONCLUSION

The results presented above demonstrate that the ICP-MS instrument provides superior results for REEs from microwave multi-acid digestion. This suggests that ICP-MS is the more effective analytical technique for REE analysis in this context. With the use of CRMs, a comparison was made for the results obtained from ICP-MS and ICP-OES techniques using CGL 111, CGL 124, and AMIS0276 to validate the reliability of these methods. The recovery percentage (%) from ICP-MS showed a good percentage yield (80 – 120%) compared to the ICP-OES instrument (50 – 120%). The ICP-MS data indicate that all fly ash samples have a high concentration of LREEs and a lower concentration of HREEs. Excellent recovery was obtained by ICP-MS in a developed microwave acid digestion method, which demonstrated excellent sensitivity, low detection limits, a wide dynamic range, and the capability for accurate multi-element analysis; thus confirming its suitability for this purpose. From all three acquired fly ash samples, REEs were successfully recovered. The samples showed similar concentration levels for all the elements. All three samples showed a high concentration level of LREEs (Y, La, Ce, and Nd) ranging between ~50 ppm to ~200 ppm, whereas the HREE (Sm, Eu, Tb, Gd, Dy, Ho, Er, and Yb) concentration was lower throughout all samples, ranging between ~0.5 ppm to ~20 ppm, as illustrated in Figure 5.

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Tshilidzi Rampfumedzi is a scientist in the Analytical Chemistry Division (ACD). I joined Mintek in 2020 as an intern, then appointed as a scientist. Upon joining ACD, I trained in various sections such as instrumentation, where I gained experience in doing elemental analysis in ICP OES and ICP- MS. I also gained experience in sample preparation for various methods and standard preparation. I also joined the Fire Assay section where I gained experience in all fire assay methods and trace methods. I am a technical signatory (TS) in PGMs and REEs methods. Currently, I am registered with Wits University for a PhD degree.