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Tetrafluoroboric Acid Digestion for Accurate Determination of Rare Earth Elements in Coal and Fly Ash by ICP-MS Analysis

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Abstract: Coal and coal-related fly ash often contain rare earth elements (REEs) that have the potential to be utilized as valuable mineral resources. Accurately determining the REE content in coal and fly ash is crucial for resource evaluation. The conventional approach involves using hydrofluoric acid (HF) to dissolve silicates and release REEs, which, however, prolongs the digestion process due to the additional step of complexing fluoride ions (F^-) with boric acid (H_3BO_3). Determining the correct amount of H_3BO_3 for neutralization can be challenging, and in some instances, the binding of fluoride ions with certain lanthanides (Lns) hampers the accurate determination of all 14 naturally occurring rare earth elements in a single digestion batch by inductively coupled plasma mass spectrometry (ICP-MS). In this study, we present an alternative method that achieves the accurate determination of all 14 naturally occurring REEs using tetrafluoroboric acid (HBF_4) followed by ICP-MS analysis. This approach eliminates the need for an F^- complexing step. We tested this method on certified REE reference materials, including NIST 1632e (coal) and NIST 1633c (fly ash), as well as the REE geological reference material USGS AGV-1 (andesite). Our results demonstrated excellent recovery rates (relative standard deviation, RSD < ±10%), with a correlation coefficient (r^2) exceeding 0.99. Using this method, we investigated the concentrations of all 14 REEs in coal and fly ash samples collected from various locations in the southwestern USA. This improved digestion technique streamlines the analysis process and enhances the accuracy of REE determination, facilitating a more comprehensive evaluation of REE-rich coal and fly ash deposits for resource exploration.

Keywords: coal ash; REEs; tetrafluoroboric acid

1. Introduction

Rare earth elements (REEs), or lanthanides (Lns), a group of elements with unique properties and pivotal roles in various high-tech industries, are found in nature in relatively low concentrations. These elements are commonly present in accessory minerals within a diverse array of geological formations, including silicates, oxides, carbonates, phosphates, halides, and other compounds, distributed across a wide spectrum of igneous, metamorphic, and sedimentary rocks within the Earth's crust [1,2]. REEs predominantly accumulate in deposits associated with alkaline igneous formations, specifically in carbonatite and pegmatite veins, and are often divided into light rare earth elements (LREEs: La, Ce, Pr, Nd, Sm, and Eu) and heavy rare earth elements (HREEs: Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu). In general, the abundance of LREEs is higher than that of HREEs according to the Oddo–Harkins effect [1,3]. These deposits serve as the primary sources for these valuable elements, and their precise characterization is indispensable in strategic resource planning and management. In recent years, the demand for REEs has surged, driven by their critical role in the development of clean energy technologies, such as solar cells, wind turbines, energy-efficient lighting, and electric vehicles. Consequently, there is an

increasing emphasis on exploring alternative sources of these elements. Notably, studies have unveiled substantial concentrations of not only REEs but also other rare metals like germanium, gallium, selenium, lithium, and yttrium within coal deposits worldwide [4,5]. This revelation has led to a concerted effort to investigate the potential of coal and coal-combustion byproducts as a viable source of REEs. The U.S. Department of Energy (DOE) and the National Energy Technology Laboratory (NETL) have initiated a comprehensive assessment of U.S. coals and coal-related materials, presenting a promising avenue for REE extraction and utilization [6].

To determine the concentrations of REEs in coal and fly ash samples, a commonly employed method involves the utilization of hydrofluoric acid (HF) to dissolve refractory constituents, especially silicates [7]. However, the HF method is recognized for its time-intensive nature, as it requires the addition of H_3BO_3 to complex the excess fluoride ions (F^-), introducing contaminants and significantly elevating the acidity of samples. This increased acidity complicates the matching of calibration standards. Moreover, the presence of a substantial amount of excess F^- in the digested solution can lead to the formation of calcium fluoride (CaF_2) precipitates, which co-precipitate some REEs [8]. The solubility of CaF_2 increases with decreasing pH due to an elevated concentration of H_3BO_3, attributed to the formation of the BF_3OH^- complex [9]. Furthermore, the HF digestion method has been observed to promote the formation of aluminum fluoride (AlF_3), which co-precipitates REEs, leading to lower recovery rates and reduced accuracy [10]. Various other techniques have been utilized in sample preparation for REE analysis [11–16], such as hot-plate acid digestion, dry-ashing, and lithium or sodium fusion. The hot-plate method is a convenient setup for digesting coal fly ash and geological materials [11–13]; however, it is important to note that the procedure can be time-consuming, particularly when dealing with samples containing the REE-bearing mineral zircon. Moreover, significant amounts of HF and HNO_3 are released into the air during the drying process, rendering this method environmentally unfriendly and economically impractical, especially for the digestion of a large number of samples. The ashing method, ASTM UOP407-09, is employed to determine certain metal concentrations in samples with substantial organic matter, such as food [14,15]. However, the ashing products of coals share similarities with fly ash. To completely liberate the REEs, an additional step, such as microwave acid digestion, is required to dissolve refractory constituents in the ash. The sodium peroxide sintering method has been employed to digest geological materials and fly ash samples in cation and trace metal analysis. However, a limited study on REE analysis suggests that this method may produce unreliable results [11,16].

It is crucial to determine the exact amount of H_3BO_3 needed to neutralize the excess F^-, but this poses a challenge as the amount of H_3BO_3 required is often excessive. For instance, the American Society for Testing and Materials (ASTM) procedure (D6357) for dissolving coal fly ash involves the use of aqua regia and a substantial amount of HF, followed by the addition of concentrated nitric acid. However, this method may not yield accurate results for all 14 REEs, as demonstrated by a recent round-robin interlaboratory study on REEs [7]. Additionally, it has been observed that the HF method falls short in providing a complete quantitative recovery of all 14 REEs, often requiring the incorporation of multiple methods, as indicated by the analysis performed by the National Institute of Standards and Technology (NIST). Notably, the NIST REE values for the fly ash standard 1633c remain incomplete, with certification achieved for only 9 out of the 14 REEs. Similarly, the NIST REE values for the coal standard 1632e could only be certified for two REEs (Ce, Eu), while the remaining REE values are solely utilized for informational purposes. In this study, we demonstrate an alternative approach that offers a solution to the limitations associated with the HF method. We present a method that ensures the accurate determination of all 14 rare earth elements in coal and coal-related fly ash samples. Our approach involves the use of fluoroboric acid (HBF_4) microwave digestion followed by inductively coupled plasma mass spectrometry (ICP-MS) analysis, providing a more efficient and comprehensive solution

for REE analysis in these materials. HBF_4 was used for digesting soil [17] and plant samples [18–20] for trace metal analysis.

2. Method Development and Materials

To assess the efficacy of the HBF_4 acid digestion method, we employed the REE standard reference materials (SRM) NIST 1632e (coal) and NIST 1633c (fly ash), as well as the geological reference material USGS AGV-1 (andesite) [21] (Table 1). We examined coal and fly ash samples obtained from various locations in the southwestern United States to determine their REE concentrations using the HBF_4 method. The coal samples were ground using a mortar and pestle. The resulting powder was sieved to achieve a particle size of less than 74 μm. Fly ash samples (PFA78480 and Escalante E-2) collected from two power plants exhibited an extremely fine particle size, measuring less than 50 μm as confirmed by SEM examination. Prior to use, the fly ash samples were ground and subsequently sieved. Approximately 30 to 40 mg of powdered coal or fly ash sample was accurately weighed for the acid digestion after shaking the sample vial to ensure homogenization. The REE reference materials and coal and fly ash samples underwent digestion utilizing the PerkinElmer Microwave Preparation System (MPS, PerkinElmer Titan MPS, PerkinElmer, Waltham, MA 02451, USA), specifically the PerkinElmer Titan MPS. Subsequently, the digested samples were subjected to analysis using the PerkinElmer ICP-MS NexIon 300s (PerkinElmer, Waltham, MA 02451, USA).

Table 1. REE concentrations in standard reference materials.

Element		Symbol	Standard Reference Materials, REE Concentration in PPM		
			NIST 1632e, Coal	NIST 1633c, Fly Ash	USGS Agv-1, Andesite
LREE	Lanthanum	La	7 *	87	38
	Cerium	Ce	12.24	180 *	67
	Praseodymium	Pr	1.5 *	-	7.6
	Neodymium	Nd	6 *	87 *	33
	Samarium	Sm	1 *	19 *	5.9
	Europium	Eu	0.2457	4.67	1.64
HREE	Gadlinium	Gd	1 *	-	5
	Terbium	Tb	0.2 *	3.12	0.7
	Dysprosium	Dy	1 *	18.7	3.6
	Holmium	Ho	0.2 *	-	0.67
	Erbium	Er	0.7 *	-	1.7
	Thulium	Tm	0.1 *	-	0.34
	Ytterbium	Yb	0.6 *	7.7 *	1.72
	Lutetium	Lu	0.1 *	1.32	0.27

*, for information only; -, not available.

2.1. Field Sites and Samples

The coal and fly ash samples that were used for the REE mineral resource investigation were collected from various field sites in the southwestern United States (Table 2).

The selection of field sites for coal sample collection was influenced by the fact that these sites supply the coals used by the respective power plants. Figure 1 shows a map of the sampling locations. The base map was modified from Hoffman, 2000 [22]. The coal-related fly ash samples were collected from San Juan Generating Station and Escalante Station, which use local coals for electricity generation. Before conducting the HBF_4 digestion experiment, we analyzed the major cation concentrations in the two fly ash samples (PFA 78480 and Escalante E-2) using XRF (Rigaku, ZSX Primus II). The predominant component in the fly ash samples is SiO_2, constituting 62.24% for PFA 78480 and 59.42% for Escalante E-2. The second highest constituent is Al_2O_3, accounting for 25.85% in PFA 78480 and 25.51% in Escalante E-2, with measured Ba concentrations of 1201 ppm and 1318 ppm, respectively.

Table 2. Coal and fly ash samples and field information.

Site	Sample ID	Material	Location	Coordinates
1	SJ-780501	Coal	San Juan coal mine	36.801° N, 108.431° W
2	FC-1 SRMG	Coal	Four corner, Salt River Material Group	36.686° N, 108.481° W
2	PFA78480	Fly ash	San Juan Generating Station	36.802° N 108.439° W
3	Escalante E-2	Bottom ash	Escalante, Plains Electric Generating and Transmission Coop	35.416° N, 108.083° W
5	EL Sequndo E-1	Coal	EL Sequndo mine, owned by Peabody Energy	35.10° N, 107.51° W
6	K3-Raton	Coal	Coal mine, Raton, NM	36.903° N, 104.439° W
6	ORP R6	Coal	Coal mine, Raton, NM	36.903° N, 104.439° W
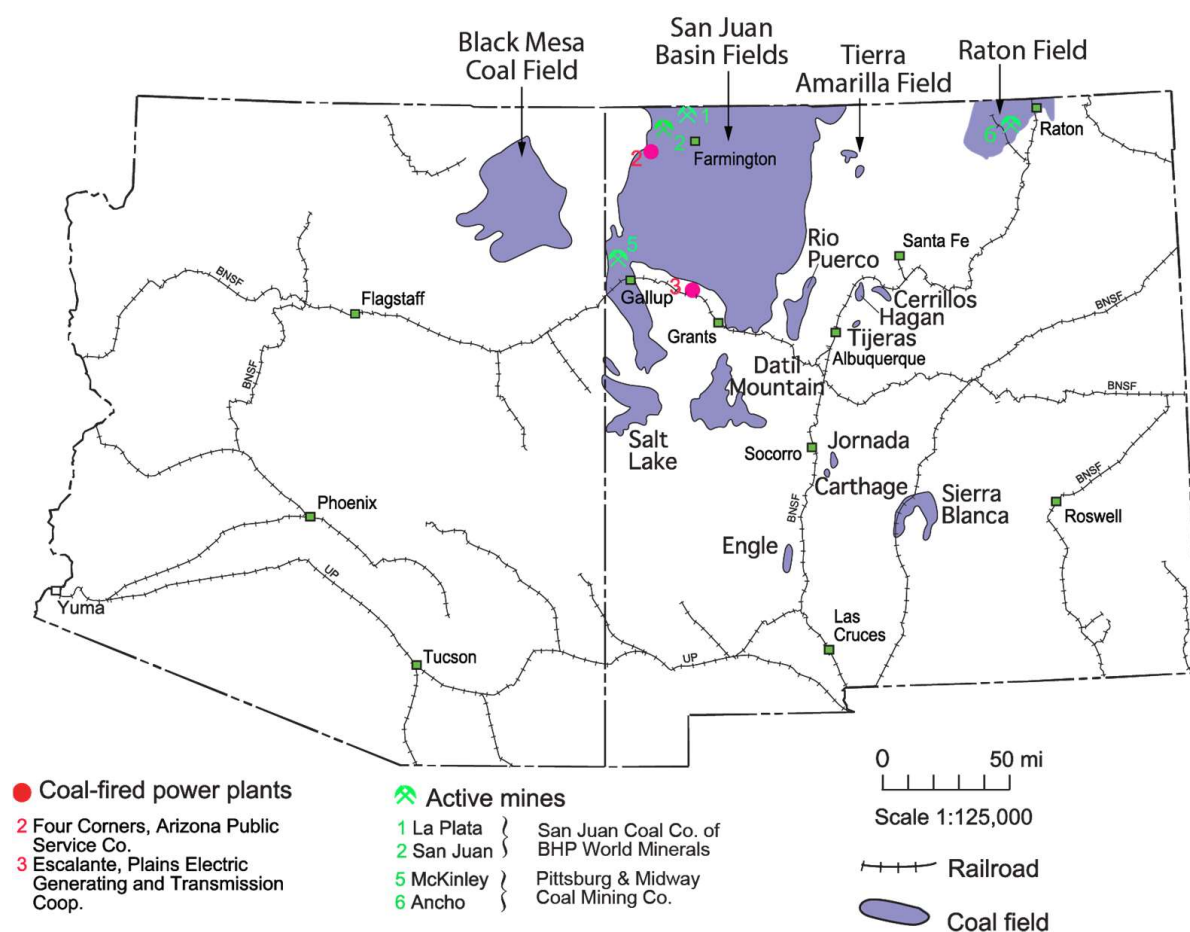
Figure 1. Field sampling sites of coal (green mill signs) and fly ash for REE determination (red dots). Base map was modified from Hoffman, 2000 [22].

2.2. Preparation of Tetrafluoroboric Acid (HBF$_4$) Solution

Unlike HF, HBF$_4$ is not acutely toxic. It does not release F$^-$ ions at the same concentration as HF because the fluoride in HBF$_4$ is bound and requires hydrolysis to yield F$^-$, resulting in approximately 100 times less F$^-$ in the HBF$_4$ solution [23]. Due to the significant contamination of commercial tetrafluoroboric acid reagents with REEs, we prepared our own tetrafluoroboric acid stock solution using boric acid (B(OH)$_3$) and hydrofluoric acid (HF) via the following procedure: B(OH)$_3$ + 4HF → H$_3$O$^+$ + BF$_4^-$ + 2H$_2$O. The boric acid (99.999% trace metals basis, CAS Number: 10043-35-3) was procured from Sigma Aldrich, and the hydrofluoric acid (TraceMetal^{TM} Grade, Fisher Chemical^{TM}, CAS number: 7664-39-3) was obtained from Fisher Scientific. To prepare the tetrafluoroboric acid solution, we added 26 g of hydrofluoric acid for every 10 g of boric acid. Once the reaction was

complete, any excess $B(OH)_3$ was allowed to settle, and we decanted the pure HBF_4. The HBF_4 was then stored in a Teflon bottle. Prior to the use of the HBF_4, a PerkinElmer ICP-MS NexIon 300s was used to verify its purity.

2.3. Microwave Acid Digestion

Microwave acid digestion (MAD) is a widely employed method for completely dissolving rock samples, aqueous samples containing suspended particles, and various sediments in order to determine trace metal concentrations, as described in [24–26]. The United States Environmental Protection Agency (EPA) Method 3052 outlines a procedure for the total digestion of solid samples containing siliceous and organic materials, using a combination of HNO_3 and HF (http://www.epa.gov/sites/production/files/2015-12/documents/3052 .pdf, accessed on 31 December 1996). In our work, we developed a microwave digestion protocol employing HBF_4 as the primary dissolution reagent, closely following the EPA method. This methodology was carried out using a PerkinElmer Titan MPS microwave sample preparation system. For each digestion, approximately 30 to 40 mg of powdered coal or fly ash sample was accurately weighed and placed into a pre-cleaned 75 mL PTFE reaction vessel. Next, 2 mL of hydrogen peroxide (H_2O_2) was added. The purpose of the H_2O_2 was to partially oxidize certain organic constituents, reducing the buildup of CO_2 during high-temperature digestion. Following a 30 min reaction period, 5 mL of nitric acid (HNO_3, Optima) and 1 mL of HBF_4 were introduced into the vessel. The reaction vessel was left open for an additional 30 min to allow for further reaction. It was then capped and placed into the Microwave Acid System (MAS) for the microwave acid digestion process. Detailed microwave settings are presented in Table 3. Following microwave digestion, 10 mL of deionized water was used to rinse the vessel to ensure the collection of all solutions.

Table 3. Settings for coal and fly ash acid digestion using PerkinElmer Titan MPS microwave sample preparation system.

Temperature (°C)	Pressure (bar)	Ramp Time (min)	Hold Time (min)	Microwave Power %
150	30	8	10	50
190	30	8	15	50
220	30	8	15	50
50	30	1	5	0
20	30	0	0	0

2.4. ICP-MS Instrumentation for REE Measurement

Inductively coupled plasma mass spectrometry (ICP-MS) is commonly utilized for determining the concentration of REEs. This is achieved by measuring one or more isotopes of the REE following the generation of positively charged REE ions in high-frequency inductively coupled argon plasma, as described in [27]. Almost all REEs exhibit one or more MO^+ interferences, with the exception of Pr, as noted in both [28,29]. In principle, the isotope with the highest relative abundance is chosen for ICP-MS analysis if it is free from isobaric or oxide interferences. However, in reality, many of these isotopes are susceptible to either isobaric or oxide interferences, as pointed out in [28,29]. Therefore, the selection of REE isotopes for ICP-MS analysis should be undertaken with careful consideration. Table 4 provides a list of the REE isotopes that we employed for REE analysis, while Table 5 outlines the operational conditions for REE concentration analysis using a PerkinElmer Nexion 300S ICP-MS.

The PerkinElmer Nexion 300S ICP-MS is equipped with universal cell technology and operated under standard mode and kinetic energy discrimination (KED) mode with helium gas as the collision cell gas. An indium internal standard (5 µg/L) was co-analyzed with the samples. As shown in Table 4, the following isotopes were chosen for ICP-MS measurements: ^{139}La (99.91%), ^{140}Ce (88.45%), ^{141}Pr (100%), ^{143}Nd (12.18%), ^{147}Sm (14.99%), ^{151}Eu (47.81%), ^{153}Eu (52.19%), ^{157}Gd (15.65%), ^{159}Tb (100%), ^{163}Dy (24.90%), ^{165}Ho (100%),

^{167}Er (22.93%), ^{169}Tm (100%), ^{173}Yb (16.13%), and ^{175}Lu (97.40%). The Eu isotopes ^{151}Eu and ^{153}Eu were monitored for BaO interference (^{135}Ba^{16}O$^+$ and ^{137}Ba^{16}O$^+$). The instrument sensitivity was tuned daily to maximize the ion counting rate prior to analysis. The tuning solution contained 1 ppb Ce and In, giving a sensitivity of ~77,000 cps for Ce and ~81,000 cps for In. Instrument optimization was carried out through standard performance checks by minimizing CeO$^+$ and Ce^{++} formation with the CeO/Ce (156/140) ratio set to ≤ 0.025 and that of Ce^{++}/Ce (70/140) set to ≤ 0.03. The optimization operations involved tuning for the nebulizer gas flow, torch alignment, torch sampling depth, QID STD/DRC, and KED cell entrance voltage, among others. A 5-point external calibration curve (0, 1, 2, 5, and 10 μg/L) was utilized to encompass the sample pulse counting range. If some of the sample ion counts exceeded the calibration range, the samples underwent further dilution to bring the ion counts within the calibration range. A typical dilution ratio ranges from 1:50 to 1:100. The concentrations of REEs in the samples were determined by applying the external calibration curve. This curve was analyzed in triplicate for each REE, and the regression coefficients exceeded 0.999.

Table 4. REE isotopes for the determination of REE concentrations using PerkinElmer Nexion 300S ICP-MS.

REEs	Suitable Isotopes	Interference (MO$^+$, MOH$^+$) *	Isobaric Overlap (M$^+$)	Correction	
La	^{139}La (99.91%)	-	-	-	
Ce	^{140}Ce (88.45%)	-	-	-	
Pr	^{141}Pr (100%)	-	Monoisotope	-	
	^{143}Nd (12.18%)	-	-	-	
Nd	^{144}Nd (23.8%)	-	^{144}Sm (3.07%)		−0.204803 * ^{147}Sm
	^{146}Nd (17.2%)	^{130}BaO		-	
Sm	^{147}Sm (14.99%)	^{130}BaOH		-	-
	^{152}Sm (26.75%)	^{136}CeO, ^{136}BaO, ^{135}BaOH		^{152}Gd (0.2%)	−0.012780 * ^{157}Gd
Eu	^{151}Eu (47.81%)	^{135}BaO, ^{134}BaOH		-	
Gd	^{157}Gd (15.65%)	^{141}PrO			
	^{160}Gd (21.86%)	^{144}SmO, ^{144}NdO		^{160}Dy (2.34%)	−0.093976 * ^{163}Dy
Tb	^{159}Tb (100%)	^{143}NdO		Monoisotope	
Dy	^{163}Dy (24.90%)	^{147}SmO		-	
	^{164}Dy (28.18%)	^{148}SmO, ^{148}NdO		^{164}Er (1.61%)	−0.047902 * ^{166}Er
Ho	^{165}Ho (100%)	^{149}SmO		Monoisotope	
Er	^{166}Er (33.61%)	^{150}SmO, ^{150}NdO		-	
	^{167}Er (22.93%)	^{151}EuO			
	^{168}Er (26.78%)	^{152}SmO, ^{152}GdO		^{168}Yb (0.13%)	−0.005955 * ^{172}Yb
Tm	^{169}Tm (100%)	^{153}EuO		Monoisotope	
	^{171}Yb (14.28%)	^{155}GdO		-	
Yb	^{173}Yb (16.13%)	^{157}GdO			
	^{174}Yb (31.83%)	^{158}DyO, ^{158}GdO		^{174}Hf(0.16%)	−0.192815 * ^{178}Hf
Lu	^{175}Lu (97.40%)	^{159}TbO		-	

* Data were compiled from Longerich et al., 1987 [17], and Raut et al., 2005 [18].

Table 5. PerkinElmer Nexion 300S ICP-MS operation conditions.

Parameters	Conditions
RF power, W	1600
Plasma gas flow (L/min)	18
Nebulizer gas flow (L/min)	0.89
Auxiliary gas flow (L/min)	1.2
Replicates per sample	3
Mode of Operation	Collision/KED (He gas)
REE Calibration Standard (ppb)	0, 1, 2, 5, 10
Ce^{2+}/Ce (70/140)	$\leq$0.03
CeO/Ce (156/140)	$\leq$0.025
Internal standard	Indium

3. Results and Discussion

3.1. Recovery of REE Concentrations in Standard Reference Materials

The concentrations of REEs in NIST reference materials (1632e coal and 1633c fly ash) were determined through the microwave digestion method, and the results are presented in Table 6. To assess the reliability of our sample preparation and analysis protocol, the USGS REEs reference material AGV-1 was analyzed as an unknown. Table 6 illustrates that the REE concentrations obtained using our HBF_4 method closely match the published values, confirming the accuracy of our approach. Figure 2 shows the excellent recovery rate obtained for the REEs from coal, fly ash, and geological reference material andesite using the HBF_4 method in a wide REE concentration range, demonstrating that HBF_4 can be used as a substitute for HF when digesting coal and fly ash, as well as geological materials, for the determination of REE concentrations. The HBF_4 method is less hazardous and provides on-demand F^- for digesting silicates.

Table 6. REE concentrations of NIST and USGS reference materials obtained using our HBF_4 method, compared with the published reference values, ppm.

Sample Id	Material		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1632e	Coal	This study	6.59	13.41	1.57	5.87	1.22	0.29	1.37	0.20	1.21	0.24	0.79	0.19	0.64	0.14
		NIST	7.00	12.24	1.50	6.00	1.00	0.25	1.00	0.20	1.00	0.20	0.70	0.10	0.60	0.10
1633c	Fly ash	This study	79.22	177.34	21.21	87.18	19.67	4.39	21.15	3.12	17.45	3.51	10.38	1.37	8.26	1.20
		NIST	87.00	180.00	-	87.00	19.00	4.67	-	3.12	18.70	-	-	-	7.70	1.32
agv-1	Andesite	This study	41.01	73.15	8.74	32.97	6.33	1.83	5.77	0.92	3.86	0.71	2.08	0.27	1.84	0.26
		USGS	38.00	67.00	7.60	33.00	5.90	1.64	5.00	0.70	3.60	0.67	1.70	0.34	1.72	0.27

Note: 1632e and 1633c are NIST REE reference material. Agv-1 is USGS REE reference material.
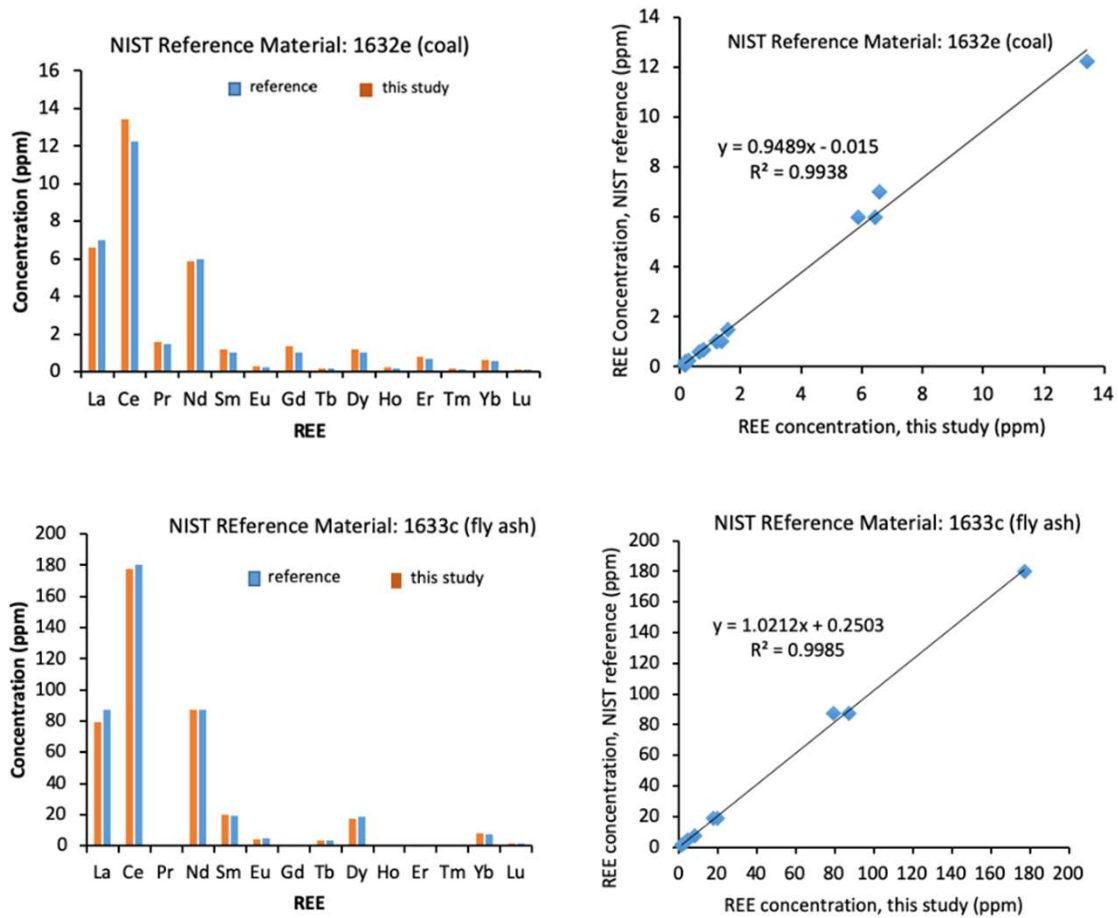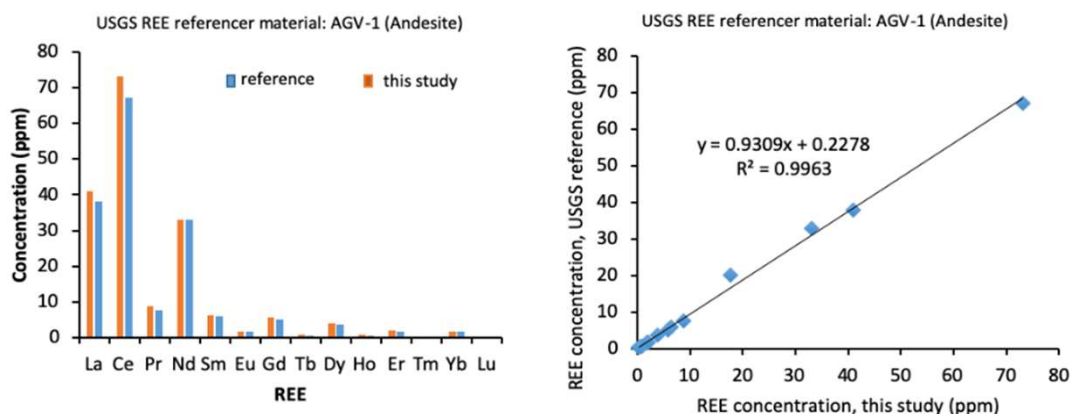

Figure 2. *Cont.*

Figure 2. Excellent recovery rate of REEs in NIST coal, fly ash, and geological material (andesite) using HBF_4 as acid digestion reagent. A, NIST 632e coal, containing low concentration of REEs, demonstrating the capability of recovering trace levels of REEs. B, NIST fly ash, demonstrating the capability of recovering high level of REEs (hundreds ppm). C, USGS andesite, demonstrating the capability of accurate determination of REEs in geological samples.

3.2. REE Concentrations of Coal and Fly Ash from SW USA

The coal and fly ash samples obtained from the southwestern (SW) USA underwent analysis via the HBF_4 digestion protocol, and the results are presented in Table 7. These findings illustrate a significant disparity in REE concentrations between fly ash samples from coal-burning power plants and coals sourced from the SW USA. The outcomes suggest a notable enrichment of REEs following coal combustion. The two coal-burning power plants utilized coal extracted from nearby mines, featuring an average REE content of 67.7 ppm, closely aligning with the global coal average of 68.5 ppm [30]. Notably, the highest REE content in coal was detected in Raton, New Mexico, registering at 105 ppm (Figure 3).

Table 7. REE concentrations (ppm) in coal and fly ash from SW USA.

Sample ID	Material	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
PFA 78480	Fly ash	64.08	126.08	15.30	57.27	9.54	1.85	8.69	1.22	7.44	1.46	4.37	0.65	5.02	0.60
Escalante E-2	Bottom ash	41.89	83.41	9.20	34.01	6.44	1.43	6.09	0.91	5.48	1.09	3.26	0.46	2.86	0.42
K3-Raton	Coal	22.89	47.52	4.93	17.02	3.14	0.77	2.85	0.41	2.46	0.45	1.22	0.18	1.07	0.18
ORP R6	Coal	29.52	34.80	3.08	11.27	1.67	0.47	2.37	0.36	2.50	0.62	1.95	0.28	1.73	0.27
SJ-780501	Coal	15.11	28.81	3.21	11.47	2.05	0.42	1.96	0.28	1.73	0.34	1.03	0.16	1.04	0.16
FC-1 SRMG	Coal	13.99	25.97	2.83	10.50	1.89	0.39	1.81	0.25	1.58	0.32	0.98	0.15	0.91	0.14
El Segundo E-1	Coal	10.35	21.71	2.20	8.13	1.50	0.33	1.51	0.27	1.24	0.25	0.81	0.13	1.79	0.14

The two fly ash samples show significantly elevated total ΣREE concentrations, with the sample from San Juan Generation Station (PFA 78480) measuring 303.57 ppm and that from Escalante (Escalante E-2) measuring 196.93 ppm, whereas the average total ΣREE in nearby coal is 67.7 ppm. Notably, all samples exhibit a very similar light rare earth element-to-heavy rare earth element (LREE/HREE) ratio, with no significant difference observed between fly ash and coal samples—8.943 for fly ash and 8.849 for coal. This suggests that coal burning did not cause REE fractionation between the LREE and HREE.

3.3. Supply of Fluoride through BF_4^- for Dissolution of Silicates

The mixing of HF and H_3BO_3 in an aqueous solution triggers an instantaneous reaction, leading to the formation of HBF_3OH (Equation (1)). Subsequently, a slower reaction ensues,

involving the initially formed complex and hydrofluoric acid, ultimately resulting in the generation of fluoroboric acid (Equation (2)).

$$H_3BO_3 + 3HF \rightarrow HBF_3OH \tag{1}$$

$$HBF_3OH + HF \rightleftharpoons HBF_4 + H_2O \tag{2}$$

The above equations can be written as follows:

$$H_3BO_3(aq) + 4HF(aq) \rightleftharpoons BF_4^- + 3H_2O + H^+ \tag{3}$$
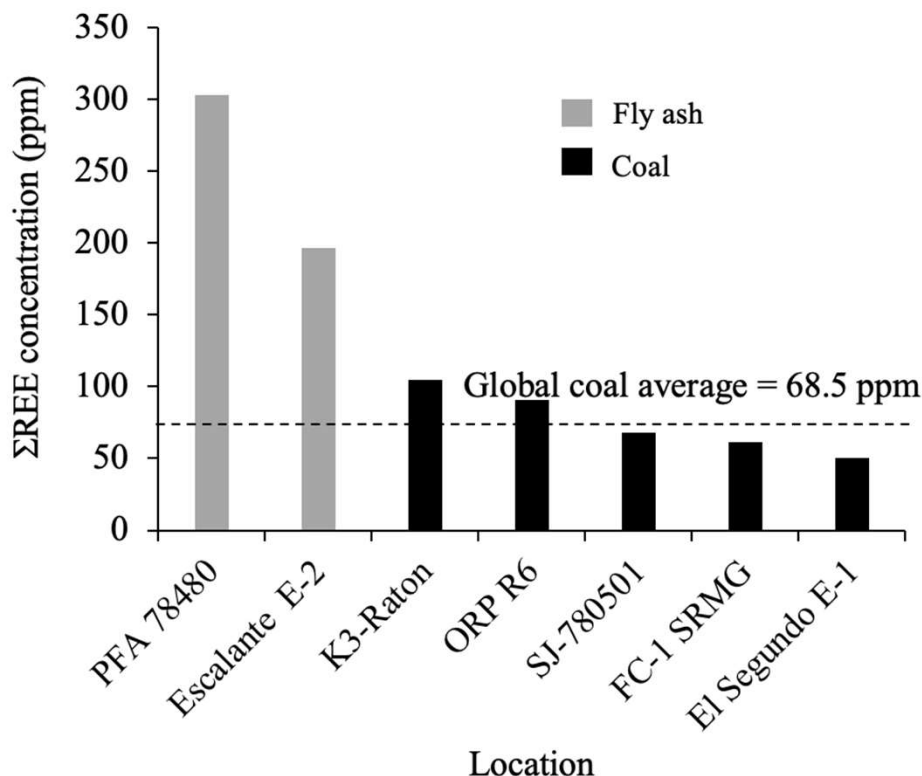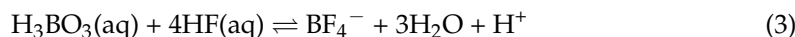
Figure 3. Total SREE concentration in coal and fly ash from SW USA, showing significant enrichment of REEs in fly ash. The dashed line indicates the global average of REEs in coal, which is 68.5 ppm [30].

At room temperature (25 °C), log k is 5.3325, the activity of H_3BO_3 (aq) is $10^{\hat{}0}$, and the activity of BF_4^-, HF, and H^+ in solution is illustrated by the following equation:

$$5.333 = \log a[BF_4^-] - 4 \log a[HF(aq)] + 3 \log a[H_2O] + \log a[H^+] \tag{4}$$

BF_4^- hydrolysis has been elucidated through the temperature-dependent equation established in [9]: $BF_4^- + H_2O \rightleftharpoons BF_3OH^- + HF$. The degree of HBF_4 hydrolysis rises with increasing temperature. Upon the dilution of HBF_4 with H_2O, the overall acidity gradually escalates, reaching a final equilibrium value. The hydrolysis of the fluoroborate ion unfolds as follows [31]:

$$BF_4^- + 3H_2O \rightleftharpoons H_3BO_3 + 3H^+ + 4F^- \tag{5}$$
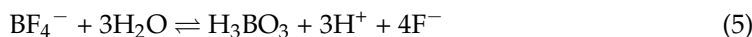
Consequently, a hydrolyzed solution encompasses HF, H_3BO_3, and HBF_4. This reaction underscores the capacity of HBF_4 to supply on-demand F^- ions for the dissolution of silicates. In general, REEs (lanthanides, Lns) are typically present as Ln^{3+} cations in acidic solution. However, their solubility undergoes a notable decrease with rising pH. This phenomenon is illustrated by the example of LaF_3 solubility in water, which is determined

to be 1.8×10^{-3} g/L [32]. Therefore, an excess of F^- in the solution promotes the shift of the equilibrium equation to the left.

4. Conclusions

The accurate determination of REEs in coal and coal-related fly ash requires the complete liberation of REEs within the silicate mineral structure. A common protocol for this is HF dissolution assisted by a microwave oven. However, the HF method is time-consuming, and it is not possible to determine all 14 REEs in the same digestion batch. We have devised a singular analytical approach capable of precisely determining the concentrations of all 14 REEs. This method represents an improved strategy for obtaining a comprehensive set of REE values in the SMRs, which is essential for accurately assessing REE resources. We have demonstrated that the use of HBF_4 provides on-demand F^- for silicate dissolution. This method has shown excellent recovery rates of REEs in coal and coal-related fly ash, as evidenced by the analysis of NIST and USGS reference materials (NIST 1632e coal and NIST 1633c fly ash). These materials contain a wide range of REE concentrations, from 0 to 200 ppm. This wet chemistry approach is applicable not only to coal and fly ash samples but also to geological materials. A REE geological reference material (USGS AGV-1, andesite) was co-analyzed as a check standard for quality assurance during sample preparation and analysis. Employing the refined methodology, we assessed the concentrations of REEs in coal and fly ash samples obtained from the southwestern USA. The fly ash from two coal-burning plants displayed heightened REE concentrations (excluding Y and Sc), measuring 304 ppm and 196 ppm, respectively, compared to the coal sample set. In comparison, the average REE concentration in coal samples was 75 ppm, surpassing the worldwide coal average of 68.5 ppm.

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