

REE Identification and Characterization of Coal and Coal By-products Containing High Rare Earth Element Concentrations

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Application of Field Portable X-ray Fluorescence to the Identification of
Rare-earth Elements



**U.S. DEPARTMENT OF
ENERGY**



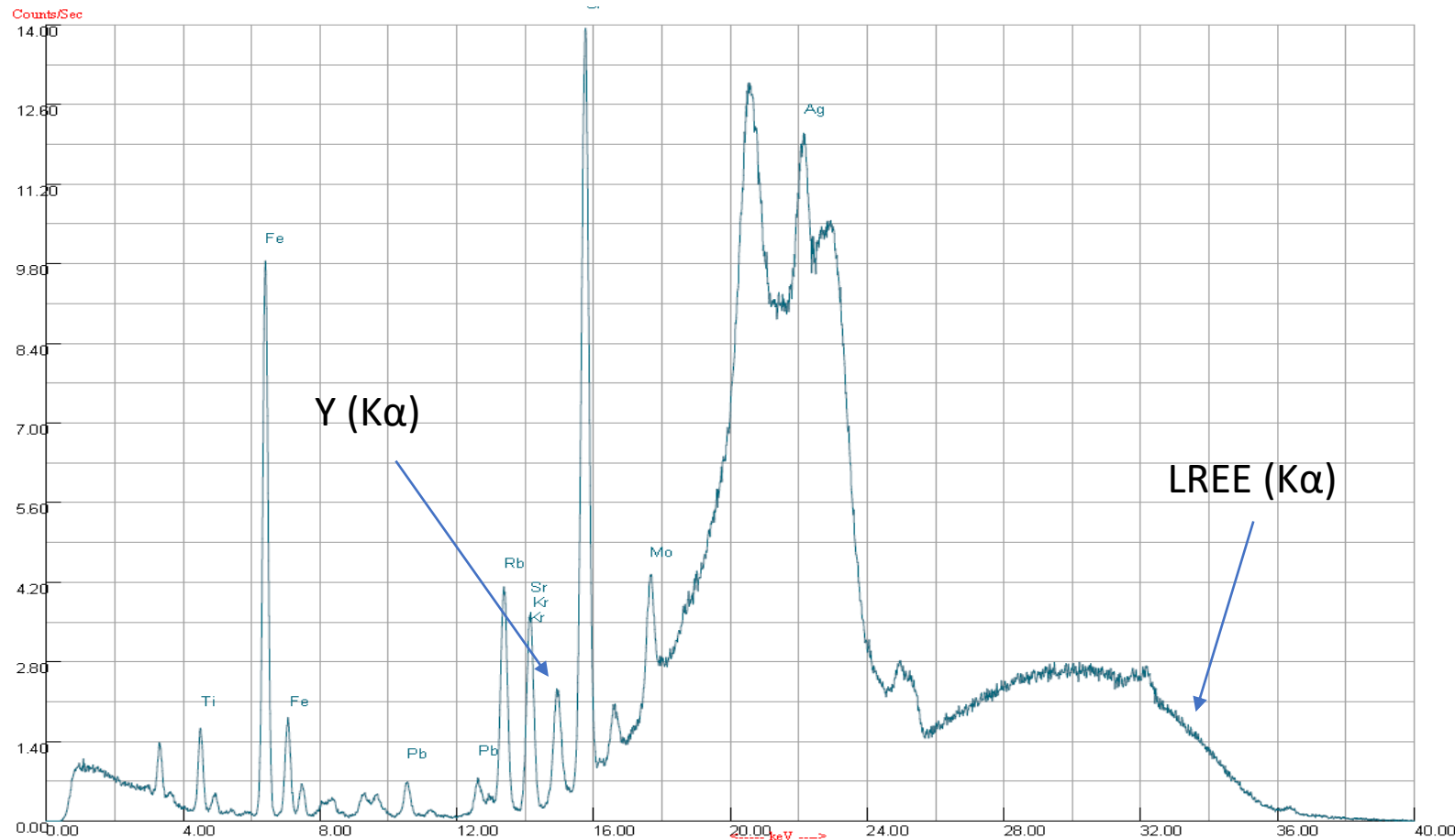
Objective

- In addition to locating samples containing >300 ppm REEs, the objective was to find a suitable technique that can be used in the field as well as the laboratory for identifying and quantifying Rare-earth Elements (REEs).
- XRF is a fast analysis technique not applied with accuracy to identifying REEs.
- A field-portable XRF device modified to detect La, Ce, Pr, and Nd was utilized for field sampling and later laboratory characterization.
- REE concentrations in coal-associated samples are often 1-10 ppm (w).
- This is well below the detection capability of the instrument, but it does allow low-concentration samples to be disregarded in the field.
- The concentration error (2σ) for the four elements is too broad to allow standard compositions to be utilized as a reference.
- A better approach turned out to be use of the measured Y concentration as a tracer.
- Samples demonstrating high REE concentrations were selected and submitted to ICP-MS analysis for correlation, and a good fit was found for Y(XRF) vs. REEs (total).

Instrument Characteristics

- **Figure 1 illustrates the XRF spectrum for a typical field sample, in this case one containing 461 ppm of REEs.**
- **When a sample contains Y, the peak at 14.96 keV appears in the spectrum.**
- **Y accompanies the other REEs at a concentration dependent upon the inorganic specie(s) containing the REEs. The species vary depending upon their association with the matrix and environment.**
- **Experimentation shows that the Y concentration typically must be on the order of 25-30 ppm to indicate total REE concentration ~ 300 ppm.**
- **Note that the $K\alpha$ values for La, Ce, Pr, and Nd lie within the backscatter portion of the XRF spectrum.**
- **The instrument's algorithm provides the numerical values for those elements, the concentrations of which are found to be lower by a factor of approximately 5X.**

Figure 1. Typical XRF Spectrum of Field Sample (EPLUJE02-15)

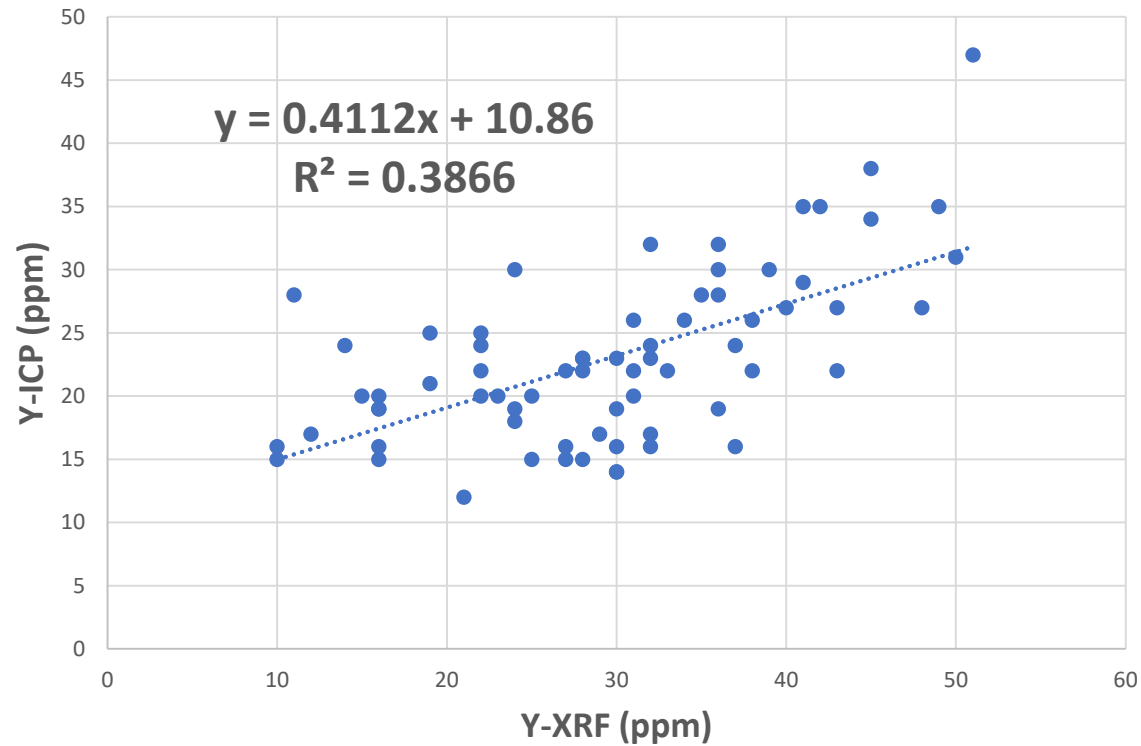


Compilation of XRF and ICP-MS Data

- Nd concentration measured by XRF at >400 ppm was usually used as a criteria to submit a sample for ICP-MS analysis.
- 79 samples were submitted for ICP-MS analysis, and 11 samples were found to contain >300 ppm total REEs. The 11-sample REE analysis is compiled in Table I.
- The XRF (2σ) values for Y concentration were found to be on the order of <5%, so the 79 Y(XRF) values were first compared to the 79 Y (ICP) values (Figure 2a),
- Knowing that Y preferentially follows HREEs, the 79 ICP-MS samples were used to compare the total HREE concentration with the Y concentration (Figure 2b).
- Knowing that the ratio of (HREE/total REE) concentration is approximately 0.1, the two comparisons were subsequently used to obtain the total expected REE concentration as a function of Y(XRF) as shown in Figure 3.
- Figure 4 represents the potential HREE concentration as a function of Y(XRF).
- Consequently, the measured Y(XRF) value can then be used as a tracer in the field to predict samples containing ~300 ppm or greater total REEs.

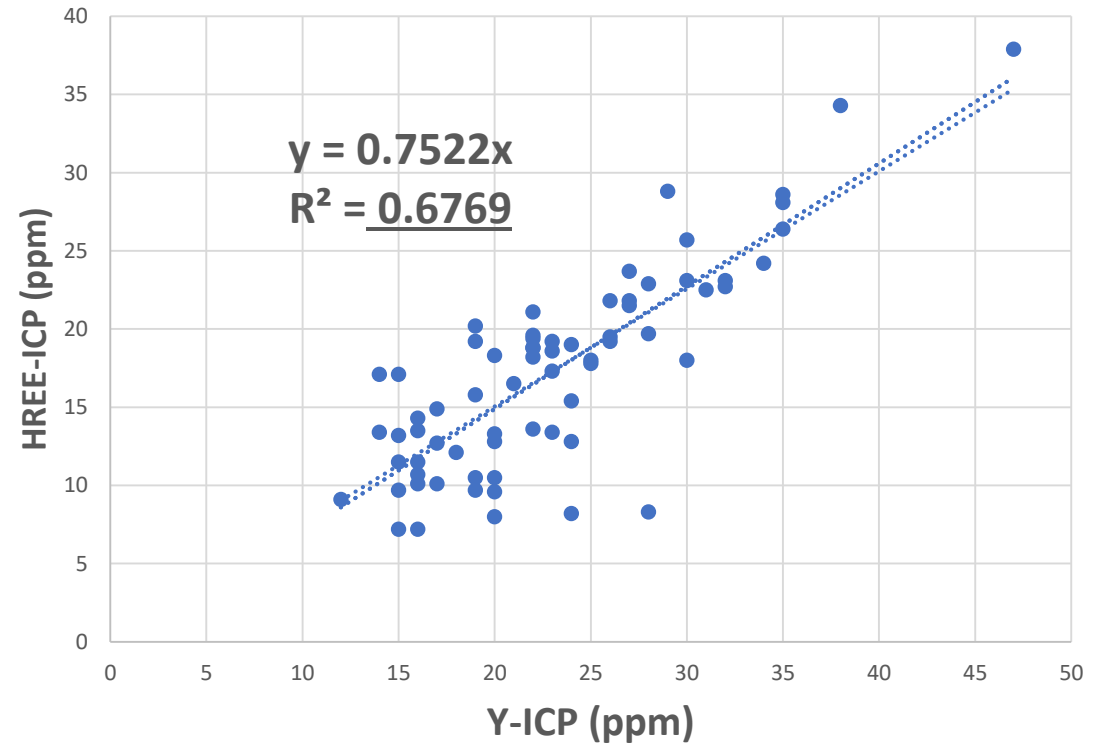
Figure 2. Combined comparison of Y(XRF), Y(ICP) and HREE(ICP)

Correlation of Y (ICP) Concentration with Y (XRF)



(a)

Correlation of total HREE Concentration (ICP) with Y



(b)

Figure 3. Calculation for Field Estimate of Total REE Concentration

Y-ICP vs. Y-XRF:

$$y = 0.4112x + 10.86$$

HREE (ICP) vs. Y(ICP):

$$Y^* = 0.7522x = 0.7522 (0.4112x + 10.86)$$

$$Y^* = 0.3093x + 8.1689 = \text{HREE ICP}$$

$$\text{HREE (ICP)} = 0.1 [\text{REE (Total)}]$$

$$\text{REE (total)} = 10 (0.3093x + 8.1689)$$

Figure 4. Correlation of HREEs (ICP) with HREEs (calculated) using Y (XRF)

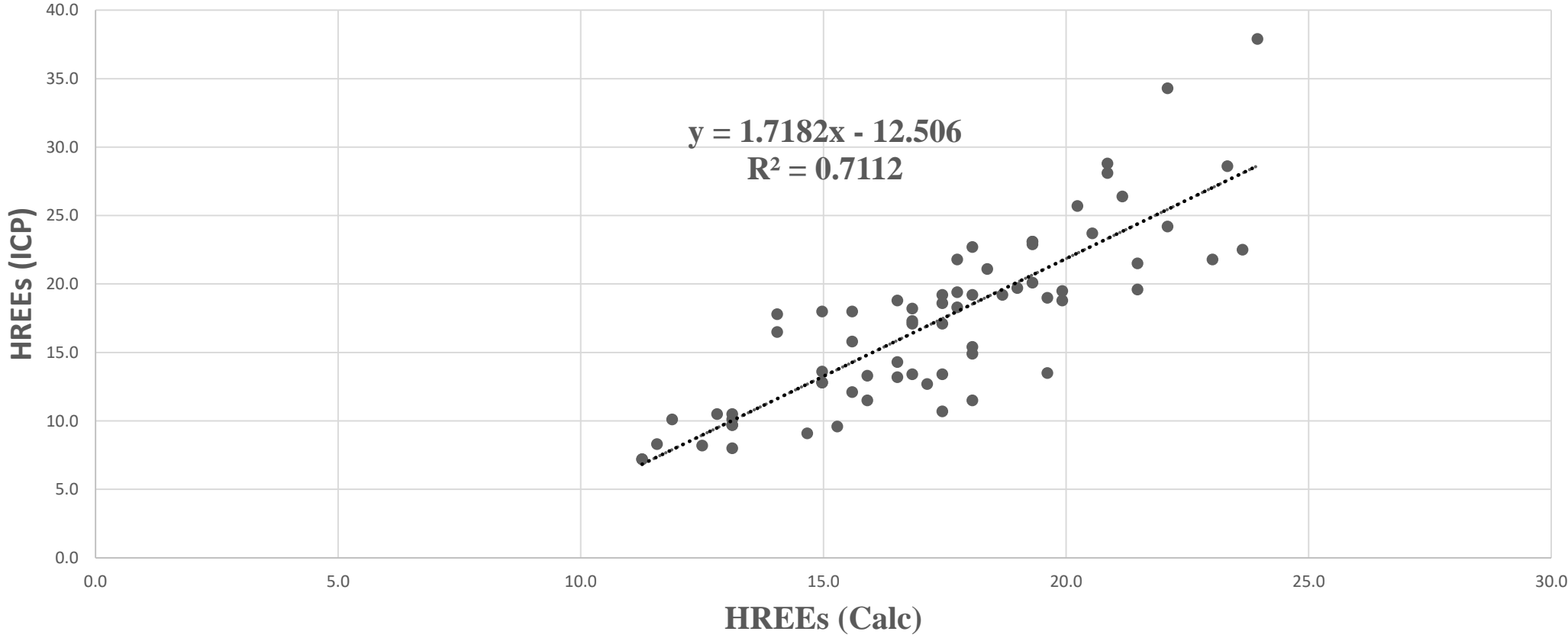


Table I: ICP-MS Chemical Analysis of Selected Coal-related Samples

Sample Number	Concentration (ppm)																Total
	La	Ce	Pr	Nd	Sm	Eu	La	Tb	Dy	Ho	Er	Tm	Yb	Lu	Sc	Y	
WPWEMA06	57	122	15	54	10	2.1	9.8	1.4	7.3	1.4	3.9	0.6	3.8	0.6	36	29	353.9
EPLUJE23	58	124	16	62	13	2.7	12	1.8	9.7	1.9	5.5	0.8	5.4	0.8	19	47	379.6
EPSCJE56	51	109	13	49	9.0	1.6	7.9	1.2	5.8	1.2	3.2	0.5	3.4	0.5	17	27	300.3
EPLUJE12	54	115	14	52	10	2.2	9.5	1.4	7.0	1.3	3.8	0.6	3.9	0.6	15	35	325.3
EPLUJE27	57	121	15	56	10	2.4	9.2	1.3	6.4	1.2	3.3	0.5	3.3	0.5	13	30	330.1
EPLUJE08	58	125	15	56	11	2.3	9.7	1.4	7.1	1.4	3.9	0.6	3.9	0.6	20	35	350.9
EPCOJE50	55	117	20	73	8.1	1.2	7.2	1.2	7.0	1.4	4.2	0.6	4.2	0.6	19	35	325.7
WPWERO07	67	130	14	47	8.1	1.8	7.7	1.1	5.1	1.0	2.9	0.5	3.0	0.5	21	26	336.7
EPLUJE15	87	176	20	73	14	3	13	1.8	8.5	1.6	4.2	0.6	4.0	0.6	16	38	461.3
WPFANU11	58	128	18	79	18	4.2	22	3.2	18	3.6	9.6	1.3	7.8	1.1	22	97	490.8
WPFANU01	35	97	16	81	26	6.6	34	4.9	25	4.3	10	1.2	6.8	1.0	34	109	491.8

Discoveries During Sample Collection and Characterization

- While there may be other tracers that can be used to locate REE concentrations of >300 ppm, a field-portable XRF device is useful for correlating the measured Y content with the potential total REE content.
- Other potential tracer elements are Ba and Th.
- Anthracite coal-associated samples are likely to contain higher REE concentrations than bituminous coal-associated samples.
- The highest REE concentrations were found in fireclays associated with bituminous coal-associated samples.
- It's difficult to identify individual, macroscopic mineral inclusions associated with REEs using SEM techniques, but phosphate-containing species were identified in anthracite-associated samples (not illustrated). This suggests an association with monazite or xenotime.
- The preponderance of samples with a sedimentary origin, the relative absence of individual mineral inclusions in samples, and the link of REEs with fireclays leads one to theorize that the species containing REEs in coal-associated samples are compacted clays. This may arise from the weathering of inorganic seams with a hydrothermal or igneous origin.