

Article

Round-Robin Interlaboratory Study on Rare-Earth Elements in U.S.-Based Geologic Materials

Bruce Folkedahl *, Carolyn Nyberg, Saptashati Biswas and Xuefei Zhang

Energy & Environmental Research Center, University of North Dakota, 15 North 23rd Street, Stop 9018, Grand Forks, ND 58201, USA

* Correspondence: bfolkedahl@undeerc.org; Tel.: +1-701-777-5243

Abstract: In a study funded by the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL), the University of North Dakota (UND) Energy and Environmental Research Center (EERC) performed a first-of-its-kind round-robin interlaboratory study (RRIS) to determine lab-to-lab and method-to-method variability in analyzing the rare earth element (REE) content of domestic resources. Analyses of REEs on eleven different materials were accomplished by the laboratories using four different procedures: ASTM D6357 (Procedure A), ASTM D4503 (Procedure B), an alternate in-house procedure for digestion and REE analysis (Procedure C), and neutron activation analysis (NAA). The results of the RRIS suggest that NAA is the most accurate and reliable method for many of the REEs in these types of materials; however, the method is limited in that it is able to determine only ten of the sixteen REEs. Five of the seven labs reporting data for Procedure A and three of the five labs reporting for Procedure B showed excellent performance in terms of repeatability, reproducibility, agreement with NAA, and SRM recoveries based on AOAC International guidelines on method performance. This indicates that when strictly followed these methods are suitable for REE determination in most materials, although are subject to the overall capabilities and experience of individual laboratories.

Keywords: rare-earth elements; round-robin interlaboratory study; ASTM methods



Citation: Folkedahl, B.; Nyberg, C.; Biswas, S.; Zhang, X. Round-Robin Interlaboratory Study on Rare-Earth Elements in U.S.-Based Geologic Materials. *Minerals* **2023**, *13*, 944. <https://doi.org/10.3390/min13070944>

Academic Editors: Pierpaolo Zuddas, Paolo Censi and Michael Zhdanov

Received: 9 March 2023

Revised: 5 July 2023

Accepted: 11 July 2023

Published: 14 July 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Rare-earth elements (REEs), which include the fourteen naturally occurring lanthanide elements of lanthanum (57) through lutetium (71) plus scandium (21) and yttrium (39), are crucial materials in an incredible array of consumer goods, energy system components, and military defense applications because of their unique properties. However, their global production and entire value chain are dominated by China [1]. While the United States currently mines and concentrates REEs, the concentrate must be shipped out of the country for further processing into discrete metals and alloys, making the United States essentially 100% import-reliant for these critical materials. Traditional mineral ores, including previously mined deposits in the United States, have several challenges. Chief among these is that the content of the most critical and valuable REEs is deficient, making mining uneconomical. Further, the supply of these critical REEs is nearly 100% produced in China from a single resource (ion-adsorbed clays) that is projected by experts to only last another 10–20 years [2–4]. The United States currently considers the REE market an issue of national security [5–7]. It is imperative that alternative domestic sources of REE be identified and that methods be developed to produce them. Recently, coal and coal byproducts have been identified as among these promising alternative resources.

The U.S. Department of Energy (DOE) has been pursuing alternative sources for REEs and critical minerals (CMs), funding multiple projects aimed at building the knowledge base and capabilities needed to advance the technology for REE and CM extraction and processing. Part of this work involves locating promising REE and CM sources and developing estimates

of resources available for processing [8]. As part of this function, determination of the precision and accuracy of commonly utilized analytical laboratory methods is an identified need. In a study funded by DOE's National Energy Technology Laboratory (NETL), the University of North Dakota (UND) Energy and Environmental Research Center (EERC) focused on identifying and quantifying REE resources associated with coal and coal-related materials in the United States. A portion of that work included a round-robin interlaboratory study (RRIS) to determine lab-to-lab and method-to-method variability in analyzing the REE content of domestic-based resources. To accomplish this, thirteen laboratories participated in an RRIS focused on analyzing REEs, a first-of-its-kind study in the United States. Analyses of REEs performed on eleven different materials were accomplished by the laboratories using four different procedures: ASTM D6357 mixed acid (i.e., hydrochloric, nitric, and hydrofluoric) digestion with heat followed by either inductively coupled plasma–mass spectrometry (ICP–MS) or ICP–optical emission spectroscopy (ICP–OES) [9]; ASTM D4503 high-temperature lithium borate fusion digestion followed by ICP–MS analysis (although this method was withdrawn by ASTM in 2012, the process has been utilized in many laboratories, and subsequent to this study ASTM has added it as an alternative preparation and analysis method to ASTM D6357) [10]; an alternate in-house procedure routinely used by one of the laboratories for digestion and REE analysis; and neutron activation analysis (NAA). This paper discusses the results of the RRIS and the statistical analysis of the results.

2. Materials and Methods

2.1. Laboratory Participants

Thirteen laboratories with the capabilities and experience to digest and analyze samples for REEs participated in the interlaboratory study. The goal was to obtain enough laboratories to provide a minimum of six datasets for each of the methods in order to meet the minimum requirement specified in ASTM E691 for determining adequate statistical precision [11]. One additional lab was selected to perform NAA as a reference method.

2.2. Sample Selection

Eleven materials were selected for the RRIS, which included a variety of sample types and matrices with varying REE concentrations. Among them were four standard reference materials (SRMs) to help determine method bias. The study materials are listed in Table 1, and the SRMs with their respective reference values are in Table 2.

Table 1. RRIS materials.

RRIS Code	Sample Type	Origin	TREE ¹ , ppm, Dry Mass Basis	Ash Content, %
Material A	Lignite coal	North Dakota/Harmon seam	400	25–30
Material B	Subbituminous coal	Wyoming/PRB ²	200	6–8
Material C	Bituminous coal	Central Appalachian	125	6–8
Material D	Bituminous fly ash	Kentucky power plant/Central Appalachian coal	700	98–100
Material E	Subbituminous fly ash	Wisconsin power plant/PRB coal	400	98–100
Material F	Clay parting	Texas/subbituminous	280	95–98
Material G	AMD ³ anthracite	Pennsylvania/Central Appalachian anthracite coal	200	50–55
Material H	Bituminous fly ash	NIST ⁴ SRM ⁵ —Pennsylvania power plant/bituminous	600	90–93
Material I	Shale	USGS ⁶ SRM—Pennsylvania Bush Creek shale	315	90–93
Material J	Bituminous coal	NIST SRM—Pennsylvania/Northern Appalachian coal	40	8–9
Material K	Mine waste material	NIST SRM—Colorado/Rocky Mountain Basin coal	190	88–92

¹ Total REE. ² Powder River Basin. ³ Acid mine drainage. ⁴ National Institute of Standards and Technology. ⁵ Standard reference material. ⁶ U.S. Geological Survey.

Table 2. SRMs included in the RRIS and REE reference values, mg/kg, dry mass basis.

Element	Symbol	NIST 1633c Fly Ash	NIST 1632e Coal	NIST 2780a Mine Waste	USGS SBC-1 Bush Creek Shale
Cerium	Ce	180	12.24	67.7	108 ± 0.9
Dysprosium	Dy	19	1	3.1	7.1 ± 0.09
Erbium	Er	–	0.7	2.0	3.8 ± 0.05
Europium	Eu	4.7	0.246	0.9	1.98 ± 0.02
Gadolinium	Gd	–	1	3.2	8.5 ± 0.1
Holmium	Ho	–	0.2	0.7	1.4 ± 0.02
Lanthanum	La	87.0	7	34.4	52.5 ± 0.6
Lutetium	Lu	1.3	0.1	0.33	0.54 ± 0.01
Neodymium	Nd	87	6	28.3	49.2 ± 0.5
Praseodymium	Pr	–	1.5	8	12.6 ± 0.1
Samarium	Sm	19	1	4.7	9.6 ± 0.1
Scandium	Sc	37.6	3.58	15.6	20 ± 0.2
Terbium	Tb	3.1	0.2	0.5	1.2 ± 0.02
Thulium	Tm	–	0.1	0.31	0.56 ± 0.01
Ytterbium	Yb	7.7	6	18	3.6 ± 0.04
Yttrium	Y	–	0.6	2	36.5 ± 0.3

2.3. Materials Preparation

The coal samples were air-dried, ground to –60 mesh (150 µm), riffled, and split according to ASTM Methods D2234 and D2013. The splits were packaged in 4 oz amber glass jars. The ash and clay materials were ground to –200 mesh (75 µm), riffled, split according to ASTM D2013, and packaged in 2 oz high-density polyethylene (HDPE) jars. The SRMs were prepared, riffled, and split by the vendors.

2.4. Homogeneity Testing

The homogeneity of the SRMs was determined by the vendors who supplied them. For the remaining materials, ten jars of each coal material were analyzed in duplicate for sulfur content and ten jars of each ash and clay material were analyzed in duplicate for silica content. All materials passed the ANOVA (analysis of variance) criteria for homogeneity with a *p*-value > 0.05. The Kruskal–Wallis statistical technique was applied to the results as well, again with a *p*-value > 0.05 [12].

2.5. Procedures and Samples Distribution

Approximately 50 g of each coal and 20 g of each of the other materials, labeled Materials A–K, were provided to each participating laboratory along with study instructions. The laboratories were asked to prepare and analyze each sample in triplicate and record the results in an Excel template that was emailed to them. They had approximately 10 weeks to complete the analysis and report the results. The study instructions are included in Appendix A.

2.6. Analytical Methods

Other than the laboratory performing NAA, the participating laboratories were asked to perform one or more of the following methods: Procedure A, ASTM D6357, mixed acid (i.e., hydrochloric, nitric, and hydrofluoric) digestion with heat followed by either ICP–MS or ICP–OES; Procedure B, ASTM D4503, high-temperature lithium borate fusion digestion followed by ICP–MS analysis; or Procedure C, an alternate procedure routinely used by one of the laboratories for digestion and REE analysis.

2.7. Statistical Methods

The data reported by the laboratories for the various procedures and test materials were compiled and the following statistics applied in accordance with ASTM Method E691,

Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method:

(\bar{X}) = average of three replicates.

s = standard deviation of triplicate test results.

RSD = ratio of the test results standard deviation (s) over the average $(\bar{X}) \times 100\%$.

S_r = repeatability standard deviation (i.e., within laboratory variability).

$$s_r = \sqrt{\sum_1^p s^2 / p} \quad (1)$$

where p is the number of laboratories and s is the standard deviation of triplicate test results.

Here, S_R is the reproducibility standard deviation (i.e., between-laboratory variability):

$$s_R = \sqrt{(s_{\bar{x}})^2 + (s_r)^2 \left(\frac{n-1}{n} \right)} \quad (2)$$

where $s_{\bar{x}}$ is the standard deviation of the test result averages, S_R is the reproducibility standard deviation, and n is the number of test results per measurement.

3. Results

3.1. Repeatability and Reproducibility

According to ASTM Method E691, the repeatability standard deviation or within-laboratory variability is defined as the standard deviation of test results obtained among the labs using the same procedure, operator, and equipment. These are considered the most favorable conditions possible and to yield the best precision of the method (i.e., the smallest standard deviation).

The reproducibility standard deviation or between-laboratory variability is determined by comparing the test results obtained with the same method on identical test materials in different laboratories with different operators using different equipment. Thus, it takes into account many more sources of variation than the repeatability does. These are considered the least favorable conditions and typically yield the worst precision of a method (i.e., the greatest standard deviation).

The repeatability standard deviation (S_r) and reproducibility deviation (S_R) were calculated for Procedures A and B, which included all sixteen elements for all eleven materials. Although only five laboratories reported data for Procedure B, which did not meet the minimum requirement according to ASTM E691, the repeatability and reproducibility were still calculated. Because only one laboratory reported results on Procedure C, the repeatability and reproducibility standard deviation could not be calculated; however, the RSDs of the triplicate values were calculated and compared to those of the other methods. One laboratory that reported data for Procedure A withdrew from the study after it discovered problems with the analysis. The data from that lab were excluded; however, the minimum number of labs for Procedure A was met. The repeatability and reproducibility results are presented in Table 3.

As expected, the between-laboratory standard deviations (S_R) were higher than the within-laboratory standard deviations (S_r). The highest (S_R) values were observed for scandium and lutetium for both procedures. In certain cases these values were as high as or even higher than the mean values. For example, the mean value (\bar{X}) from Procedure B for scandium (Sc) on Material K was 24.82 ppm and the (S_R) value was 20.8 ppm, while for lutetium (Lu) on Material K using Procedure A the mean value (\bar{X}) was 0.432 ppm and the (S_R) value was 0.733 ppm.

The repeatability or reproducibility standard deviation can be expressed as a fraction of the element concentration, which is the RSD, defined above as the ratio of the test results standard deviation (s) in ppm over the mean (\bar{X}) in ppm $\times 100\%$. Although the RSDs

for Procedure C are based on only three replicates obtained from one laboratory, this can nonetheless provide information on the within-laboratory precision of the method.

Table 3. Repeatability (within lab) and reproducibility (between lab) standard deviations, µg/g dry whole sample basis.

		Procedure A															
		Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Material A	\bar{X}	15.86	34.58	31.95	80.86	10.09	42.19	8.82	1.996	8.713	1.305	8.212	1.655	4.911	0.713	4.709	0.746
	s_r	0.468	0.658	0.716	1.60	0.193	1.16	0.279	0.0288	0.212	0.033	0.219	0.0321	0.101	0.015	0.0765	0.014
	s_R	1.91	3.44	2.55	5.69	0.827	2.39	0.560	0.227	1.32	0.233	0.934	0.183	0.436	0.056	0.340	0.13
Material B	\bar{X}	1.844	2.224	2.815	4.613	0.623	2.387	0.432	0.126	0.577	0.073	0.422	0.085	0.252	0.040	0.233	0.039
	s_r	0.0446	0.0332	0.0428	0.108	0.013	0.0343	0.0117	0.0027	0.0093	0.001	0.0054	0.002	0.0045	0.001	0.0023	0.0005
	s_R	0.790	0.418	0.334	1.51	0.057	0.185	0.130	0.036	0.327	0.010	0.043	0.011	0.026	0.009	0.030	0.006
Material C	\bar{X}	4.426	18.98	19.74	42.10	4.784	18.00	3.722	0.381	3.500	0.569	3.379	0.702	2.020	0.313	1.824	0.256
	s_r	0.187	0.539	0.813	1.86	0.204	0.808	0.163	0.015	0.152	0.018	0.110	0.022	0.0615	0.010	0.0633	0.0088
	s_R	0.530	2.57	3.16	6.46	0.763	3.06	0.490	0.055	0.66	0.075	0.431	0.066	0.219	0.072	0.2268	0.023
Material D	\bar{X}	53.61	121.48	95.55	201.73	23.65	92.55	20.61	4.391	20.49	3.325	21.31	4.406	12.45	1.929	10.88	1.589
	s_r	2.22	9.298	1.92	17.70	0.647	7.05	0.897	0.130	0.778	0.107	0.519	0.0758	0.399	0.0488	0.351	0.0411
	s_R	7.78	16.71	7.20	20.48	1.91	8.43	1.64	0.420	2.42	0.415	1.39	0.274	1.03	0.432	0.986	0.154
Material E	\bar{X}	27.67	51.98	54.04	105.03	13.23	51.54	9.907	2.712	12.85	1.546	8.998	1.824	5.309	0.742	5.062	0.749
	s_r	2.31	0.633	1.17	2.541	0.212	0.820	0.133	0.0436	0.246	0.0243	0.228	0.0534	0.0795	0.019	0.0686	0.013
	s_R	18.2	7.44	14.5	30.12	3.35	13.9	3.40	0.912	7.79	0.402	2.19	0.473	1.37	0.199	0.396	0.249
Material F	\bar{X}	5.323	31.30	53.11	110.73	11.49	41.52	7.615	0.515	6.338	0.927	5.840	1.124	3.388	0.521	3.402	0.545
	s_r	0.545	0.717	2.96	4.977	0.433	2.09	0.267	0.022	0.229	0.041	0.225	0.0489	0.128	0.022	0.123	0.026
	s_R	1.44	4.56	5.46	9.545	1.71	3.47	0.619	0.145	1.42	0.25	0.713	0.194	0.445	0.062	0.408	0.15
Material G	\bar{X}	11.56	10.37	23.18	48.38	5.558	20.60	4.206	0.938	2.991	0.437	2.401	0.457	1.496	0.219	1.461	0.260
	s_r	0.228	0.201	0.542	0.769	0.0856	0.457	0.0593	0.013	0.0520	0.018	0.0795	0.014	0.0431	0.0078	0.0339	0.011
	s_R	3.81	3.56	7.06	13.2	1.66	6.00	1.29	0.071	1.07	0.085	0.565	0.096	0.456	0.055	0.273	0.14
Material H	\bar{X}	38.53	102.01	82.10	191.29	21.91	91.26	20.52	4.465	20.11	3.124	18.31	3.348	10.02	1.456	8.608	1.549
	s_r	1.34	9.848	10.0	14.99	0.635	8.47	0.580	0.141	0.749	0.106	0.611	0.132	0.309	0.0501	0.343	0.0603
	s_R	4.29	17.09	11.2	18.02	2.05	11.2	2.19	0.502	2.66	0.373	1.79	0.669	1.03	0.274	0.878	0.798
Material I	\bar{X}	22.02	29.48	51.26	103.86	12.78	49.31	10.10	1.969	8.277	1.221	6.590	1.108	3.576	0.505	3.361	0.633
	s_r	0.439	0.919	1.66	4.501	0.309	1.70	0.343	0.0588	0.253	0.0376	0.246	0.0504	0.110	0.023	0.0679	0.033
	s_R	2.39	4.15	4.25	16.81	0.890	3.50	0.678	0.173	1.50	0.170	0.594	0.248	0.405	0.054	0.306	0.35
Material J	\bar{X}	3.513	5.271	5.684	11.89	1.424	5.543	1.192	0.246	1.086	0.182	1.018	0.202	0.588	0.0895	0.557	0.123
	s_r	0.0794	0.237	0.234	0.542	0.0412	0.127	0.0209	0.0045	0.0179	0.0047	0.0186	0.0038	0.013	0.0017	0.0096	0.0022
	s_R	0.382	0.832	0.616	0.997	0.0884	0.255	0.181	0.013	0.166	0.042	0.0671	0.013	0.032	0.016	0.042	0.106
Material K	\bar{X}	14.76	6.203	29.31	53.27	6.658	23.31	4.223	0.710	2.347	0.406	1.838	0.238	1.017	0.112	0.949	0.432
	s_r	0.366	0.350	1.33	3.11	0.237	0.998	0.155	0.034	0.0871	0.070	0.0797	0.016	0.0307	0.012	0.034	0.012
	s_R	3.27	1.75	5.24	10.9	1.75	4.45	1.76	0.143	1.12	0.315	1.37	0.074	0.795	0.034	0.508	0.733

Table 3. Cont.

		Procedure B															
		Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Material A	\bar{X}	21.40	44.18	37.34	79.44	11.95	44.32	8.549	1.987	10.54	1.376	8.539	2.150	5.134	0.924	4.882	0.732
	s_r	1.27	4.04	2.56	2.22	0.870	2.93	0.280	0.0709	0.505	0.0454	0.262	0.115	0.172	0.046	0.142	0.023
	s_R	11.6	15.1	11.9	7.66	4.54	26.2	0.861	0.194	3.67	0.136	0.925	0.968	0.630	0.42	0.573	0.075
Material B	\bar{X}	2.103	2.992	3.335	6.246	0.626	3.027	0.501	0.140	0.593	0.088	0.566	0.117	0.358	0.052	0.329	0.049
	s_r	0.313	0.202	0.107	0.237	0.0065	0.126	0.0069	0.0096	0.045	0.003	0.020	0.016	0.026	0.009	0.021	0.005
	s_R	1.50	0.662	0.902	1.78	0.074	1.07	0.035	0.048	0.233	0.035	0.241	0.057	0.169	0.025	0.132	0.010
Material C	\bar{X}	5.049	23.29	22.72	48.85	5.771	19.40	4.616	0.464	4.362	0.711	4.306	0.903	2.097	0.376	2.350	0.275
	s_r	0.398	1.37	1.35	1.02	0.348	1.62	0.347	0.045	0.256	0.059	0.339	0.061	0.193	0.025	0.147	0.0067
	s_R	2.05	4.92	6.43	13.5	1.96	1.62	1.87	0.17	1.56	0.31	1.82	0.43	0.245	0.19	1.07	0.018
Material D	\bar{X}	61.85	125.86	91.53	191.56	23.32	80.79	21.03	4.568	22.09	3.643	22.85	4.695	13.64	1.911	12.23	1.869
	s_r	2.53	5.917	4.13	9.346	1.20	5.35	1.12	0.209	1.08	0.199	1.33	0.306	0.852	0.104	0.753	0.0302
	s_R	31.3	15.86	7.48	15.71	2.22	37.1	2.81	0.640	1.91	0.584	3.77	0.909	2.61	0.393	2.38	0.405
Material E	\bar{X}	29.16	53.01	60.41	117.49	14.70	50.73	12.25	2.818	11.64	1.703	10.31	2.051	5.979	0.848	5.487	0.850
	s_r	1.48	0.954	1.03	1.984	0.266	0.944	0.263	0.0760	0.288	0.0631	0.230	0.0553	0.146	0.029	0.178	0.028
	s_R	21.1	6.23	4.85	8.754	1.44	23.2	1.49	0.410	1.07	0.293	1.88	0.409	1.17	0.17	1.02	0.18
Material F	\bar{X}	4.616	32.55	53.16	107.19	11.88	43.48	7.774	0.575	6.811	1.030	6.476	1.287	3.855	0.568	3.858	0.576
	s_r	0.212	0.864	0.909	1.519	0.214	0.805	0.161	0.051	0.139	0.0196	0.121	0.0375	0.0709	0.025	0.102	0.025
	s_R	1.58	4.32	5.86	11.36	1.42	4.80	1.20	0.11	0.544	0.237	1.23	0.256	0.789	0.12	0.871	0.14
Material G	\bar{X}	16.80	19.35	25.15	50.31	5.921	19.54	4.553	0.966	4.288	0.625	3.881	0.776	2.267	0.325	2.153	0.326
	s_r	0.748	0.753	0.640	1.17	0.108	0.702	0.194	0.049	0.190	0.041	0.143	0.043	0.123	0.011	0.132	0.010
	s_R	12.2	3.28	3.18	5.59	0.661	9.88	0.654	0.15	0.316	0.15	0.557	0.13	0.381	0.0534	0.348	0.050
Material H	\bar{X}	44.36	101.57	79.57	176.61	21.86	80.43	20.64	4.619	21.57	3.242	19.61	3.885	10.94	1.479	9.307	1.416
	s_r	2.86	2.688	2.07	4.515	0.562	1.05	0.408	0.168	0.573	0.105	0.576	0.113	0.302	0.0339	0.144	0.0345
	s_R	22.5	11.32	8.51	18.27	2.86	35.0	3.68	0.816	2.83	0.684	4.19	0.907	2.41	0.345	2.08	0.370
Material I	\bar{X}	26.83	33.19	49.40	103.57	12.38	51.20	9.884	1.996	8.726	1.258	7.309	1.399	4.091	0.578	3.813	0.584
	s_r	0.725	0.884	1.02	2.479	0.310	1.35	0.238	0.0586	0.198	0.0366	0.298	0.0653	0.164	0.039	0.169	0.029
	s_R	17.9	4.02	4.58	8.175	1.19	4.35	1.40	0.283	0.824	0.195	1.29	0.272	0.753	0.12	0.635	0.13
Material J	\bar{X}	3.669	5.384	5.226	10.46	1.258	4.973	1.022	0.248	1.065	0.188	0.995	0.228	0.622	0.118	0.553	0.085
	s_r	0.530	0.172	0.243	0.470	0.068	0.184	0.106	0.076	0.099	0.087	0.076	0.087	0.110	0.094	0.079	0.002
	s_R	2.05	1.78	1.38	2.83	0.251	1.17	0.195	0.068	0.167	0.082	0.163	0.082	0.109	0.103	0.090	0.006
Material K	\bar{X}	24.82	16.99	34.43	65.17	7.531	29.69	4.714	0.907	3.435	0.496	3.164	0.684	2.156	0.327	2.175	0.375
	s_r	1.41	0.595	0.878	1.56	0.177	0.788	0.102	0.033	0.109	0.043	0.0969	0.032	0.109	0.016	0.0322	0.022
	s_R	20.8	2.14	3.32	5.22	0.770	2.96	0.687	0.136	0.335	0.090	0.614	0.150	0.413	0.088	0.445	0.093

The mean repeatability (within-laboratory) relative standard deviations for Procedures A, B, and C are summarized and compared in Table 4 and Figures 1 and 2.

Table 4. Mean repeatability RSD for all RRIS materials and elements (%).

	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Tb	Lu	Mean—All Elements
Material A	2.0	1.7	2.1	1.7	1.7	2.1	2.1	1.3	1.9	2.5	2.0	1.8	1.8	2.0	1.4	1.7	1.9
Material B	2.2	1.0	1.3	2.6	1.9	1.6	2.0	1.6	1.6	1.4	1.0	2.0	1.7	3.2	0.9	1.1	1.7
Material C	3.3	2.6	3.5	3.7	3.4	3.6	3.6	3.5	3.6	7.2	2.9	10.0	2.6	7.6	2.7	2.7	4.2
Material D	3.5	5.3	1.8	5.0	2.0	5.4	3.4	2.3	3.3	2.7	2.0	1.5	2.4	2.1	2.6	2.0	3.0
Material E	4.7	2.2	1.3	1.6	1.6	1.6	1.5	1.6	1.8	1.5	2.3	2.1	1.7	2.7	1.7	1.8	1.9
Material F	5.3	2.0	4.3	3.5	2.6	3.5	2.6	4.6	2.5	4.3	2.7	3.6	2.7	3.5	2.4	3.5	3.4
Material G	1.7	1.6	2.2	1.3	1.4	2.0	1.7	1.3	1.7	2.2	2.3	2.4	2.0	1.6	1.5	1.8	1.8
Material H	2.6	4.6	7.6	4.0	2.2	5.0	2.1	2.1	2.8	2.4	2.6	2.6	2.2	2.6	2.7	3.2	3.2
Material I	1.8	2.7	2.4	3.9	2.0	2.5	2.8	2.5	3.0	2.5	2.9	4.5	2.7	3.4	1.7	3.1	2.8
Material J	2.2	3.9	3.3	3.1	2.3	2.1	1.7	1.6	1.7	2.0	1.6	4.2	2.1	1.6	1.5	1.6	2.3
Material K	2.2	5.0	3.3	4.9	2.8	3.1	3.1	4.0	3.5	5.3	4.2	6.4	2.6	7.6	3.6	5.2	4.2
Mean—All Materials	2.9	3.0	3.0	3.2	2.2	3.0	2.4	2.4	2.5	3.1	2.4	3.7	2.2	3.4	2.1	2.5	
	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Tb	Lu	Mean—All Elements
Material A	5.0	4.3	3.9	3.4	3.8	3.8	4.3	4.4	3.0	3.9	3.2	3.4	3.9	3.1	3.2	3.6	3.8
Material B	11.8	3.6	1.9	2.0	0.9	6.2	2.3	4.0	2.9	3.6	2.5	4.4	3.1	7.6	3.8	5.8	4.1
Material C	7.0	3.4	3.6	3.3	3.4	5.8	3.6	4.3	3.3	3.6	3.6	3.1	3.7	3.3	3.5	4.7	3.9
Material D	4.0	3.7	3.0	3.0	3.0	4.1	3.3	3.2	3.5	3.6	3.0	3.4	3.4	3.2	3.0	3.8	3.4
Material E	2.2	1.7	1.5	1.5	1.6	2.6	2.0	2.6	2.2	3.2	2.2	2.4	2.1	3.0	2.8	2.6	2.3
Material F	3.8	2.1	1.6	1.3	1.7	1.8	1.9	6.6	2.0	1.8	1.9	2.6	1.6	4.1	2.7	3.9	2.6
Material G	4.8	3.5	2.0	1.8	1.7	5.0	2.9	3.4	3.3	5.1	2.5	3.7	3.3	3.1	3.5	2.7	3.3
Material H	4.3	2.5	2.2	2.2	2.2	1.4	1.6	3.2	2.2	2.7	2.7	2.7	2.3	2.1	1.5	2.2	2.4
Material I	2.5	2.3	1.8	2.0	2.1	3.0	2.2	2.3	2.1	2.3	2.8	3.7	2.4	5.0	3.2	4.1	2.8
Material J	21.5	3.9	4.6	4.8	4.8	4.5	7.5	13.5	6.5	15.9	6.0	14.8	9.5	18.8	8.3	22.9	10.5
Material K	4.6	3.3	2.4	2.3	2.2	10.5	2.2	3.2	3.0	6.5	2.7	4.5	3.7	4.4	1.0	4.7	3.8
Mean—All Materials	6.5	3.1	2.6	2.5	2.5	4.4	3.1	4.6	3.1	4.7	3.0	4.4	3.6	5.2	3.3	5.5	
	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Tb	Lu	Mean—All Elements
Material A	30.9	19.0	24.3	17.2	25.6	20.7	24.5	24.4	23.0	23.4	23.7	23.9	23.5	22.6	20.6	25.1	23.3
Material B	47.3	37.8	26.2	22.9	24.9	22.8	21.1	20.4	17.3	18.4	17.3	17.4	17.1	16.3	16.3	21.7	22.8
Material C	23.3	4.5	20.7	20.4	22.4	38.1	22.5	15.8	17.6	17.3	15.1	13.6	11.8	12.3	10.1	14.1	17.5
Material D	40.6	10.6	5.9	6.9	7.4	7.6	7.5	7.5	10.8	13.1	8.5	11.9	11.8	7.2	6.6	12.4	11.0
Material E	26.5	12.1	10.6	4.7	8.9	8.0	6.4	7.8	2.7	4.1	2.9	2.3	2.0	2.3	4.3	5.2	6.9
Material F	29.5	20.4	16.4	13.4	17.9	16.9	15.7	14.0	11.2	13.2	11.9	11.4	10.8	10.9	12.2	14.7	15.0
Material G	53.2	32.5	24.9	23.1	27.1	25.3	23.9	24.8	17.1	17.6	15.2	14.7	14.5	14.7	15.5	19.9	22.7
Material H	27.6	30.6	7.7	9.4	11.0	7.6	15.2	16.8	22.3	20.1	23.0	24.1	25.9	27.3	28.6	23.5	20.1
Material I	23.8	16.7	13.8	10.5	13.0	12.0	11.3	10.3	7.9	9.4	7.9	7.7	7.2	6.8	7.5	11.1	11.1
Material J	47.3	39.1	29.6	31.0	29.0	28.3	26.4	25.8	20.7	22.4	21.1	20.7	19.9	19.0	18.3	24.1	26.4
Material K	24.1	19.5	25.2	23.7	24.6	25.4	23.0	22.1	19.9	22.0	21.9	22.5	22.2	22.6	76.6	27.1	26.4
Mean—All Materials	34.0	22.1	18.7	16.7	19.3	19.3	17.9	17.3	15.5	16.5	15.3	15.5	15.2	14.7	19.7	18.1	

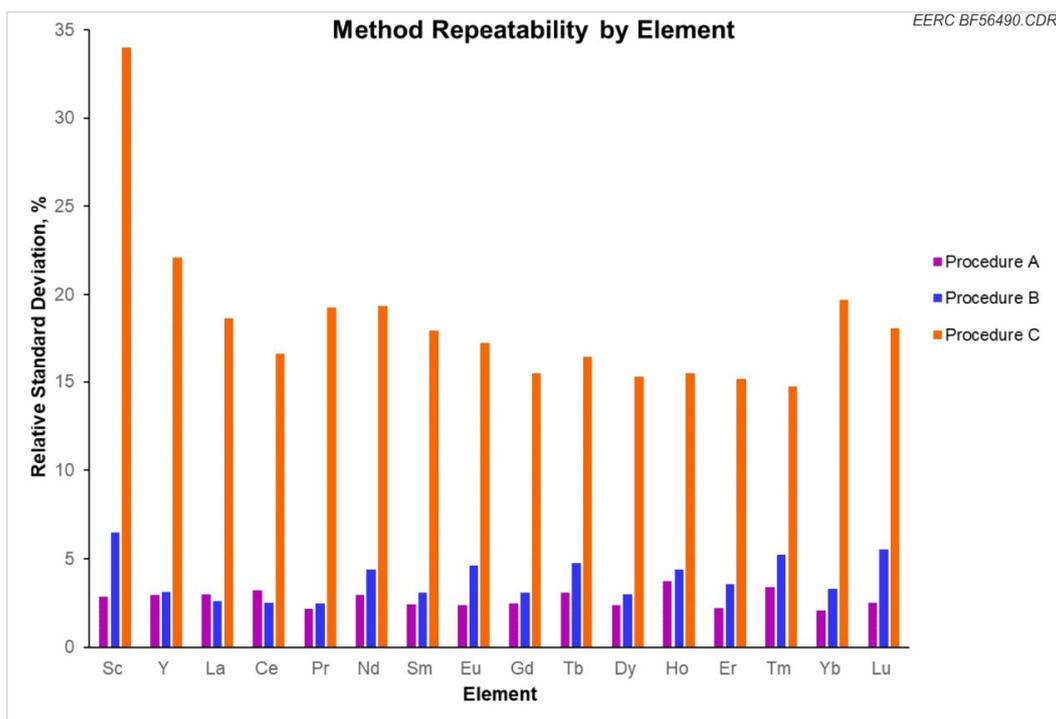


Figure 1. Method repeatability by element.

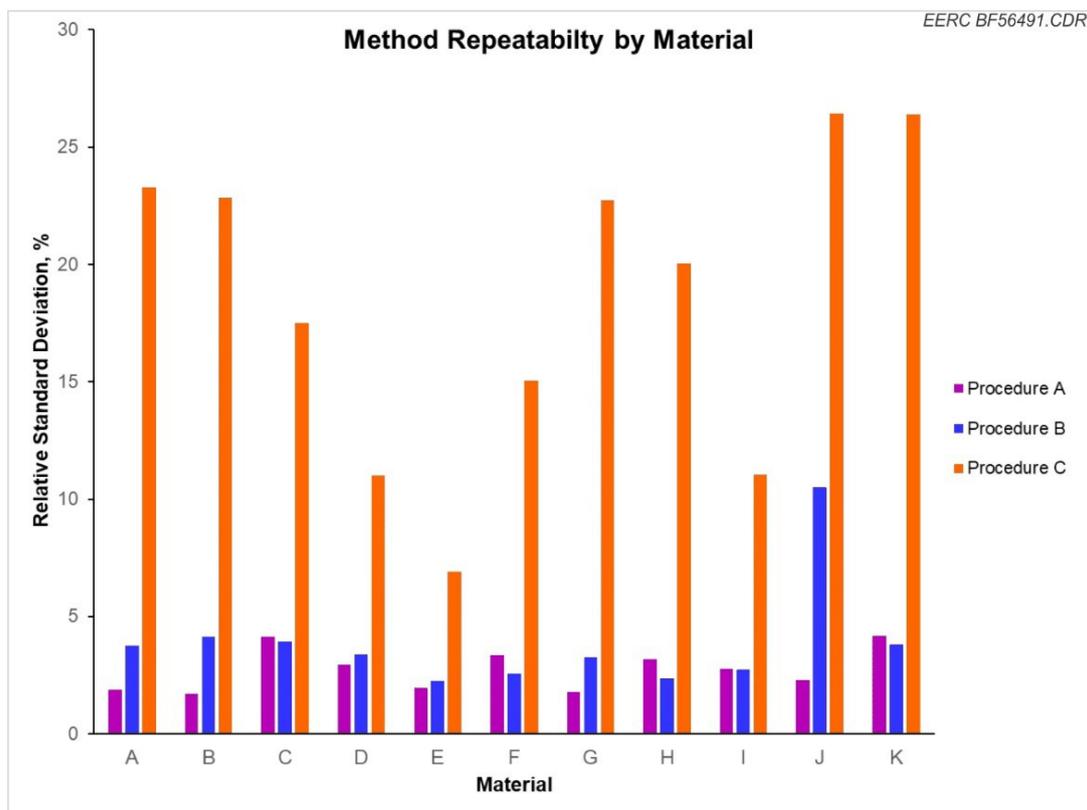


Figure 2. Method repeatability by material.

The repeatability RSD results show that Procedures A and B well outperformed Procedure C, with Procedure A slightly better than Procedure B. The overall mean RSDs by material and by element were all less than 5% for Procedure A and in all but two values

(scandium at 6.5% and Material J at 10.5%) for Procedure B. All mean RSDs calculated for Procedure C exceeded 5%, ranging from 6.9% to 34%. AOAC International reproducibility guidelines range from 15% for analyte concentrations near 100 ppb to 5% for analyte concentrations near 100 ppm [13].

The mean reproducibility (between-laboratory) RSDs for Procedures A and B are summarized and compared in Table 5 and Figures 3 and 4. As with the S_r and S_R results, these results show that the between-laboratory RSDs are much higher than the within-laboratory RSDs. The mean between-laboratory RSDs all exceeded 13%, with the highest mean value being 59% for scandium for Procedure B. AOAC International reproducibility guidelines range from 22% for analyte concentrations near 100 ppb to 8% for analyte concentrations near 100 ppm [13].

Table 5. Mean reproducibility RSD for all RRIS materials and elements (%).

Procedure A																	
	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Mean—All Elements
Material A	12.1	10.0	8.0	7.0	8.2	5.7	6.3	11.4	15.1	17.9	11.4	11.0	8.9	7.8	7.2	17.4	10.3
Material B	42.8	18.8	11.9	32.7	9.1	7.7	30.1	28.6	56.7	13.7	10.2	13.0	10.3	22.3	12.9	15.5	21.0
Material C	12.0	13.6	16.0	15.3	15.9	17.0	13.2	14.4	18.9	13.2	12.8	9.4	10.8	22.9	12.4	8.9	14.2
Material D	14.5	13.8	7.5	10.2	8.1	9.1	8.0	9.6	11.8	12.5	6.5	6.2	8.2	22.4	9.1	9.7	10.4
Material E	65.8	14.3	26.8	28.7	25.3	27.0	34.3	33.6	60.6	26.0	24.3	25.9	25.7	26.8	7.8	33.2	30.4
Material F	27.0	14.6	10.3	8.6	14.9	8.4	8.1	28.2	22.3	27.2	12.2	17.3	13.1	11.9	12.0	26.9	16.4
Material G	33.0	34.3	30.5	27.3	29.9	29.1	30.7	7.5	35.8	19.5	23.5	20.9	30.5	24.9	18.7	52.4	28.0
Material H	11.1	16.8	13.7	9.4	9.4	12.3	10.7	11.2	13.2	11.9	9.8	20.0	10.3	18.8	10.2	51.5	15.0
Material I	10.9	14.1	8.3	16.2	7.0	7.1	6.7	8.8	18.1	13.9	9.0	22.4	11.3	10.7	9.1	55.5	14.3
Material J	10.9	15.8	10.8	8.4	6.2	4.6	15.2	5.3	15.3	23.0	6.6	6.4	5.4	17.9	7.5	86.0	15.3
Material K	22.2	28.2	17.9	20.5	26.3	19.1	41.8	20.2	47.8	77.7	74.4	31.0	78.2	30.6	53.5	169.8	47.4
Mean—All Materials	23.8	17.6	14.7	16.8	14.6	13.4	18.6	16.3	28.7	23.3	18.2	16.7	19.3	19.7	14.6	47.9	
Procedure B																	
	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Mean—All Elements
Material A	54.1	34.1	31.7	9.6	38.0	59.1	10.1	9.8	34.8	9.9	10.8	45.0	12.3	45.9	11.7	10.2	26.7
Material B	71.3	22.1	27.0	28.5	11.8	35.4	7.0	34.3	39.3	39.7	42.6	48.6	47.2	48.3	40.1	20.3	35.2
Material C	40.5	21.1	28.3	27.7	34.0	8.4	40.5	37.3	35.8	43.3	42.3	47.5	11.7	49.3	45.6	6.4	32.5
Material D	50.7	12.6	8.2	8.2	9.5	45.9	13.4	14.0	8.6	16.0	16.5	19.4	19.1	20.6	19.5	21.7	19.0
Material E	72.4	11.8	8.0	7.5	9.8	45.7	12.2	14.5	9.2	17.2	18.2	20.0	19.6	20.5	18.6	21.1	20.4
Material F	34.2	13.3	11.0	10.6	12.0	11.0	15.4	19.3	8.0	23.0	19.0	19.9	20.5	21.5	22.6	24.7	17.9
Material G	72.6	16.9	12.6	11.1	11.2	50.6	14.4	15.7	7.4	23.2	14.4	16.6	16.8	16.4	16.2	15.4	20.7
Material H	50.7	11.1	10.7	10.3	13.1	43.5	17.8	17.7	13.1	21.1	21.4	23.3	22.0	23.3	22.3	26.1	21.7
Material I	66.7	12.1	9.3	7.9	9.6	8.5	14.2	14.2	9.4	15.5	17.6	19.4	18.4	20.4	16.7	22.1	17.6
Material J	55.8	33.1	26.5	27.0	19.9	23.5	19.1	27.5	15.7	43.4	16.4	36.1	17.6	87.6	16.2	7.6	29.6
Material K	84.0	12.6	9.6	8.0	10.2	10.0	14.6	14.9	9.8	18.2	19.4	22.0	19.2	26.8	20.4	24.8	20.3
Mean—All Materials	59.4	18.3	16.6	14.2	16.3	31.1	16.2	19.9	17.4	24.6	21.7	28.9	20.4	34.6	22.7	18.2	

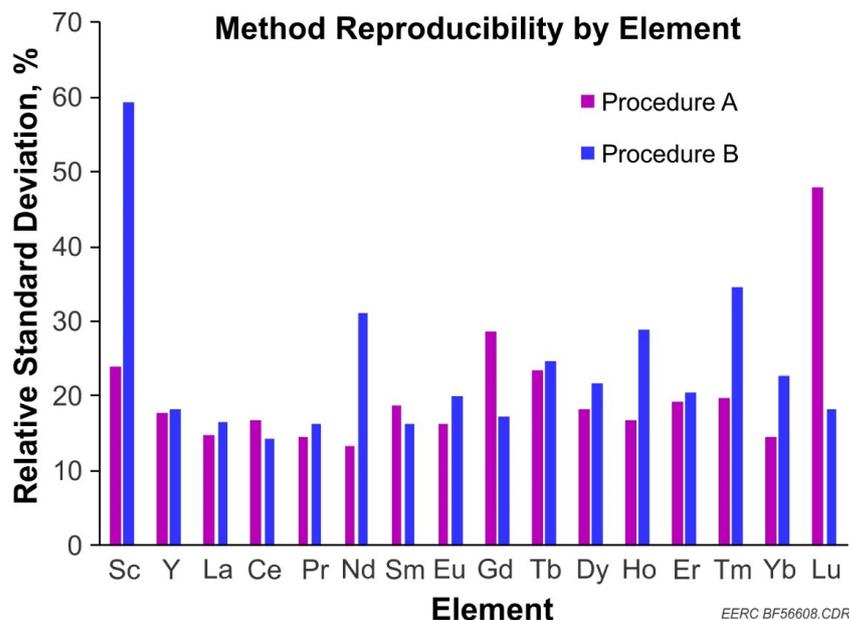


Figure 3. Method reproducibility by element.

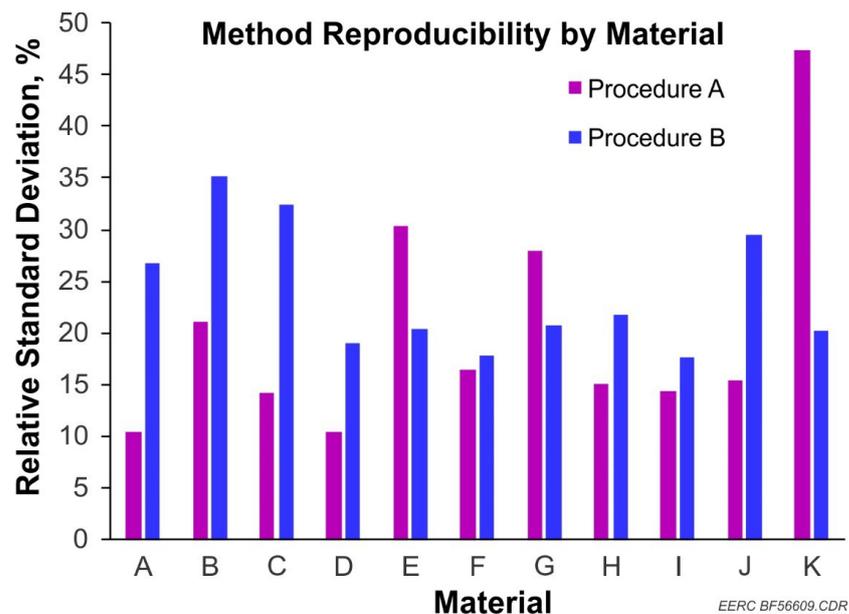


Figure 4. Method reproducibility by material.

3.2. SRM Recovery

Four SRMs, described in Table 2, were included in the study to help determine the overall accuracy and bias of the methods based on the recovery of the analyte from the matrix. The recovery was calculated by taking the average mean values (\bar{X}) reported by the labs for each of the elements and dividing by the reference value reported in the SRM certificates multiplied by 100%. The results are presented in Table 6. In terms of average recoveries, all methods showed acceptable recoveries ($\pm 15\%$) for all four SRMs, with the exception of Procedure C for Material H (78%) and Procedures A and C for Material K (67% and 73%, respectively). Although the average recoveries were reasonable, the ranges (max. and min.) for several of the procedures were large. The largest variation for all procedures was observed with Material K (46%–180%). AOAC International recovery guidelines range from 80% to 110% for analyte concentrations ranging from 100 ppb to 10 ppm and 90%–107% for analyte concentrations near 100 ppm [13].

Table 6. REE recovery from SRMs (%).

Material H										Material I									
NIST 1633c Fly Ash										USGS SBC-1 Bush Creek Shale									
Element	Reference Value	NAA		Procedure A		Procedure B		Procedure C		Element	Reference Value	NAA		Procedure A		Procedure B		Procedure C	
		\bar{X} , $\mu\text{g/g}$	Recovery, %			\bar{X} , $\mu\text{g/g}$	Recovery, %												
Sc	37.6 ± 0.6	36.5	97%	40.7	108%	44.4	118%	32.8	87%	Sc	20 ± 0.2	20.2	101%	24.4	122%	26.8	134%	34.2	171%
Y	NA ¹	NR ²	NR	89.6	NA	102	NA	107.8	NA	Y	36.5 ± 0.3	NR	NR	25.3	69%	33.2	91%	45.7	125%
La	87.0 ± 2.6	82.6	95%	72.5	83%	79.6	91%	71.7	82%	La	52.5 ± 0.6	52.2	99%	44.0	84%	49.4	94%	57.1	109%
Ce	180	186	103%	181	101%	177	98%	172	96%	Ce	108 ± 0.9	110	102%	93.9	87%	104	96%	120	111%
Pr	NA	NR	NR	19.0	NA	21.9	NA	17.9	NA	Pr	12.6 ± 0.1	NR	NR	11.0	87%	12.4	98%	13.5	108%
Nd	87	88	101%	81	93%	80	92%	78	90%	Nd	49.2 ± 0.5	47.5	96%	42.4	86%	42.0	85%	52.7	107%
Sm	19	21	109%	18	93%	21	109%	15	79%	Sm	9.6 ± 0.1	10.3	107%	8.7	90%	9.9	103%	9.8	102%
Eu	4.67 ± 0.07	4.43	95%	3.86	83%	4.62	99%	3.20	69%	Eu	1.98 ± 0.02	1.94	98%	1.97	99%	2.00	101%	1.90	96%
Gd	NA	NR	NR	17.5	NA	21.6	NA	15.2	NA	Gd	8.5 ± 0.1	NR	NR	7.1	84%	8.7	103%	8.1	95%
Tb	3.12 ± 0.06	3.21	103%	2.71	87%	3.24	104%	2.26	72%	Tb	1.2 ± 0.02	1.2	102%	1.2	102%	1.3	105%	1.1	95%
Dy	18.70 ± 0.30	17.93	96%	15.83	85%	19.61	105%	13.26	71%	Dy	7.1 ± 0.09	6.6	93%	5.7	80%	7.3	103%	6.4	90%
Ho	NA	NR	NR	2.92	NA	3.88	NA	2.61	NA	Ho	1.4 ± 0.02	NR	NR	0.96	68%	1.4	100%	1.2	88%
Er	NA	NR	NR	8.66	NA	10.9	NA	7.40	NA	Er	3.8 ± 0.05	NR	NR	3.1	81%	4.1	108%	3.6	94%
Tm	NA	NR	NR	1.26	NA	1.48	NA	0.90	NA	Tm	0.56 ± 0.01	NR	NR	0.44	78%	0.58	103%	0.50	89%
Yb	7.7	8.6	111%	7.4	97%	9.3	121%	5.5	71%	Yb	3.6 ± 0.04	3.6	100%	2.9	80%	3.8	106%	3.2	88%
Lu	1.32 ± 0.03	1.25	94%	1.55	117%	1.42	107%	0.81	62%	Lu	0.54 ± 0.01	0.55	101%	0.63	117%	0.58	108%	0.47	86%
Min			94%		83%		91%		62%	Min			93%		68%		85%		86%
Max			111%		117%		121%		96%	Max			107%		122%		134%		171%
Average			100%		95%		104%		78%	Average			100%		88%		102%		103%

Table 6. Cont.

Material J										Material K									
NIST 1632e Coal										NIST 2780a Mine Waste									
Element	Reference Value	NAA		Procedure A		Procedure B		Procedure C		Element	Reference Value	NAA		Procedure A		Procedure B		Procedure C	
		\bar{X} , $\mu\text{g/g}$	Recovery, %			\bar{X} , $\mu\text{g/g}$	Recovery, %												
Sc	3.583 ± 0.088	3.302	92%	3.513	98%	3.669	102%	5.354	149%	Sc	15.6	16.1	103%	19.5	125%	24.8	159%	28.1	180%
Y	6	NR	NR	4.7	78%	5.4	90%	7.9	131%	Y	18	NR	NR	5.51	31%	17.0	94%	18.7	104%
La	7	6.1	87%	5.0	72%	5.2	75%	6.0	86%	La	34.4	35.5	103%	26.0	76%	34.4	100%	27.7	80%
Ce	12.24 ± 0.27	12.38	101%	11.17	91%	10.46	85%	12.42	101%	Ce	67.7	68.7	102%	50.3	74%	65.2	96%	52.7	78%
Pr	1.5	NR	NR	1.2	83%	1.3	84%	1.37	92%	Pr	8	NR	NR	5.82	73%	7.53	94%	5.8	72%
Nd	6	5.6	93%	4.9	82%	4.1	69%	5.3	89%	Nd	28.3	28.6	101%	20.9	74%	23.9	85%	20.7	73%
Sm	1	1.2	118%	1.0	104%	1.0	102%	1.0	100%	Sm	4.7	4.9	105%	3.8	80%	4.7	100%	3.1	67%
Eu	0.2457 ± 0.0063	0.2428	99%	0.2142	87%	0.2483	101%	0.2086	85%	Eu	0.9	0.86	95%	0.64	72%	0.91	101%	0.6	61%
Gd	1	NR	NR	1.0	95%	1.1	107%	0.9	91%	Gd	3.2	NR	NR	2.15	67%	3.44	107%	1.9	61%
Tb	0.2	0.2	82%	0.2	79%	0.2	94%	0.1	68%	Tb	0.5	0.45	89%	0.36	71%	0.50	99%	0.3	51%
Dy	1	1.0	103%	0.9	89%	1.0	100%	0.8	83%	Dy	3.1	2.9	95%	1.6	53%	3.2	102%	1.5	49%
Ho	0.2	NR	NR	0.2	101%	0.2	114%	0.2	84%	Ho	0.7	NR	NR	0.24	34%	0.68	98%	0.3	46%
Er	0.7	NR	NR	0.5	73%	0.6	89%	0.5	71%	Er	2.0	NR	NR	0.90	45%	2.2	108%	1.0	52%
Tm	0.1	NR	NR	0.1	78%	0.1	118%	0.1	68%	Tm	0.31	NR	NR	0.10	32%	0.33	106%	0.2	50%
Yb	0.6	0.541	90%	0.5	81%	0.6	92%	0.4	72%	Yb	2	2.0	99%	0.83	41%	2.2	109%	1.9	94%
Lu	0.1	0.085	85%	0.1	123%	0.1	114%	0.1	65%	Lu	0.33	0.45	135%	0.43	131%	0.37	114%	0.17	52%
Min			82%		72%		69%		65%	Min			89%		31%		85%		46%
Max			118%		123%		118%		149%	Max			135%		131%		159%		180%
Average			95%		88%		96%		90%	Average			103%		67%		104%		73%

¹ Not available. ² Not reported.

3.3. Comparison of Methods with NAA

The results reported by the NAA reference method were compared to the data generated from the three procedures (A, B, and C). For various reasons, which include low gamma ray energies, long decay time, low sensitivity to neutrons, and no stable isotopes produced, NAA is only able to quantitatively measure ten of the sixteen REEs. These ten elements are Sc, La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, and Lu.

Figures 5–14 show the mean concentrations and standard deviations obtained from the four procedures for each of the eleven materials. The standard deviations were calculated from the following number of observations (i.e., test results): NAA ($n = 3$), Procedure A ($n = 21$), Procedure B ($n = 15$), and Procedure C ($n = 3$). Each element is presented in a separate figure.

Table 7 shows the calculated percent difference of each of the Procedures A, B, and C from the reference method NAA. The difference was calculated by subtracting the mean value of all observations obtained by each procedure from the mean value obtained by NAA divided by the mean value of NAA multiplied by 100%. A positive value shows that the mean value resulting from that procedure was higher than that of NAA, while a negative value shows that the value was lower. Values that agree within $\pm 15\%$ of the reference method are highlighted.

These results show that Procedures A and B performed significantly better than Procedure C in terms of overall agreement with NAA. Of the 110 results (10 elements \times 11 materials), Procedures A and B met the $\pm 15\%$ limit for 100 (83%) and 98 (81%) results, respectively. Procedure C performed the worst, meeting the limit for only 50 (41%) results. Scandium and lutetium were observed to have relatively high RSDs of over 60% for either Procedure A or B with respect to reproducibility of the measured quantities, whereas the RSDs for the reproducibility of the other eight REEs were less than 35%. The high RSD of these methods for lutetium can be explained by the low concentrations found in all of the materials, which impact the effectiveness of lutetium recovery, instrument detection, and quantification accuracy. Lutetium quantification values ranged from 0.04 to 1.8 $\mu\text{g/g}$. On the other hand, scandium levels were much higher, ranging from 1.2 to 61.8 $\mu\text{g/g}$, which should rule out detection limit problems.

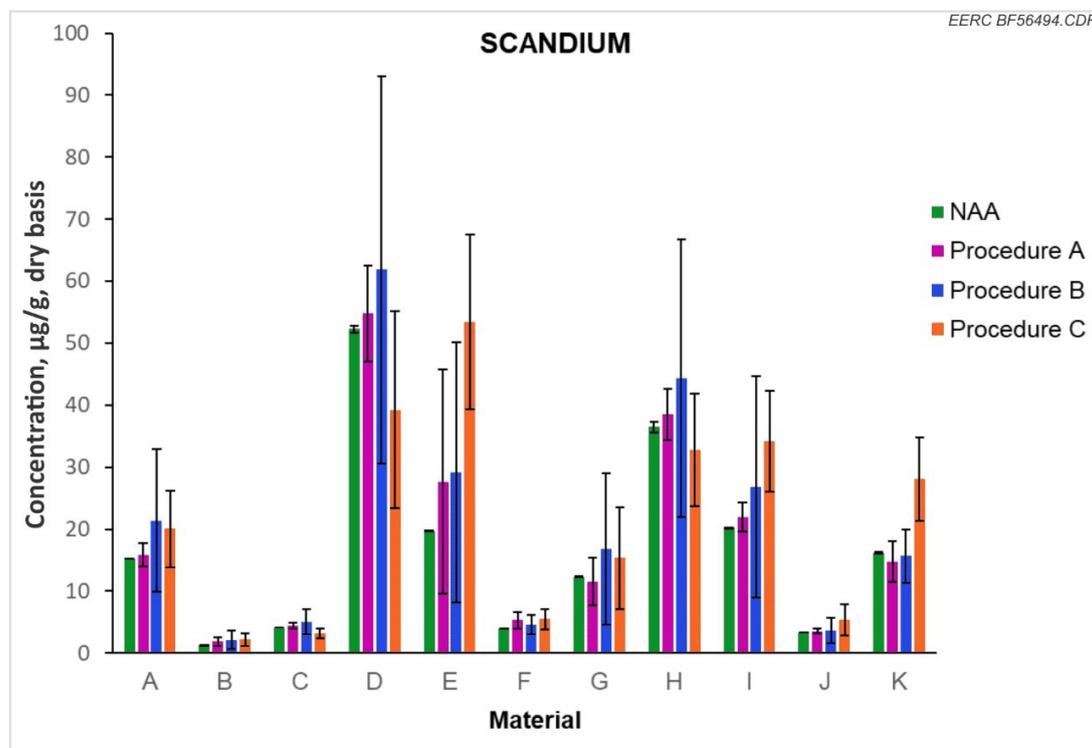


Figure 5. Mean scandium concentrations reported by the four RRIS methods.

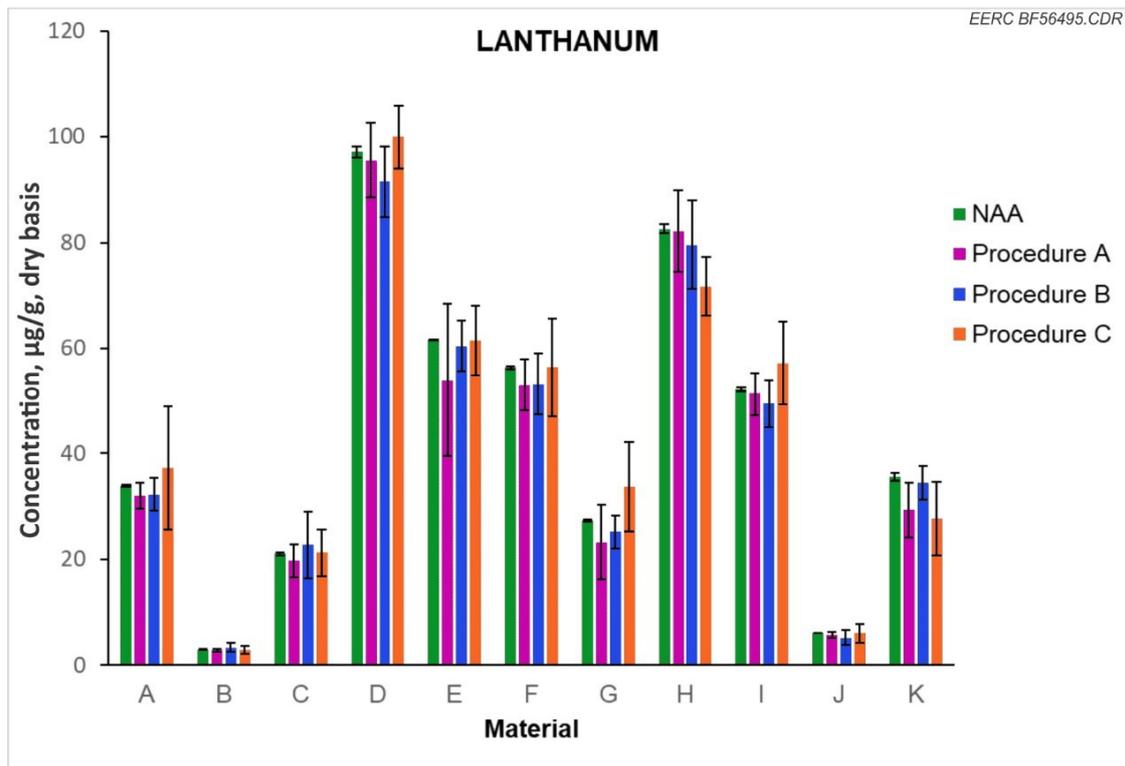


Figure 6. Mean lanthanum concentrations reported by the four RRIS methods.

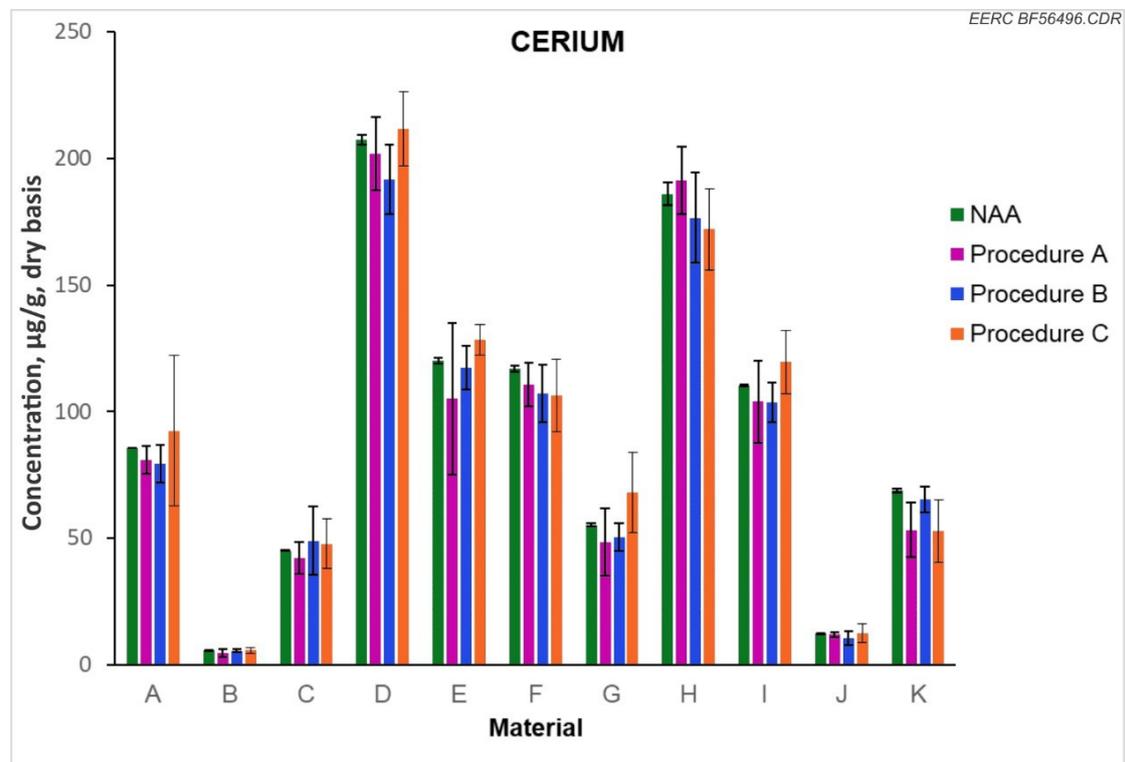


Figure 7. Mean cerium concentrations reported by the four RRIS methods.

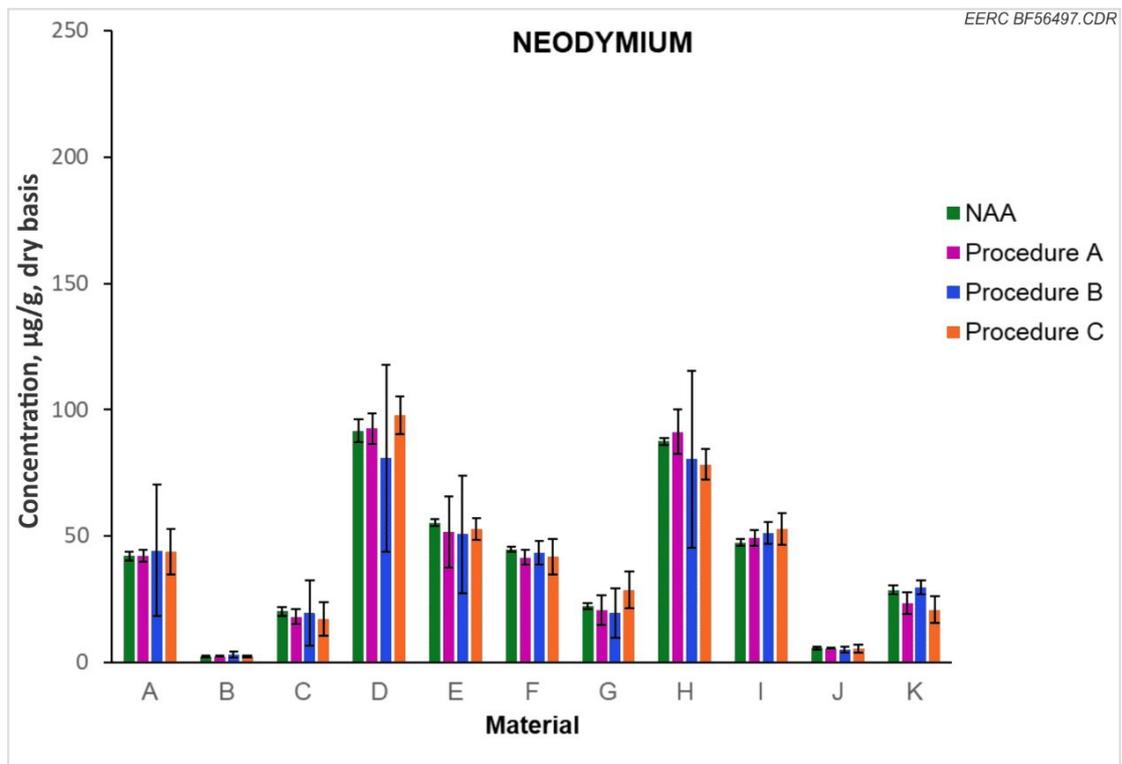


Figure 8. Mean neodymium concentrations reported by the four RRIS methods.

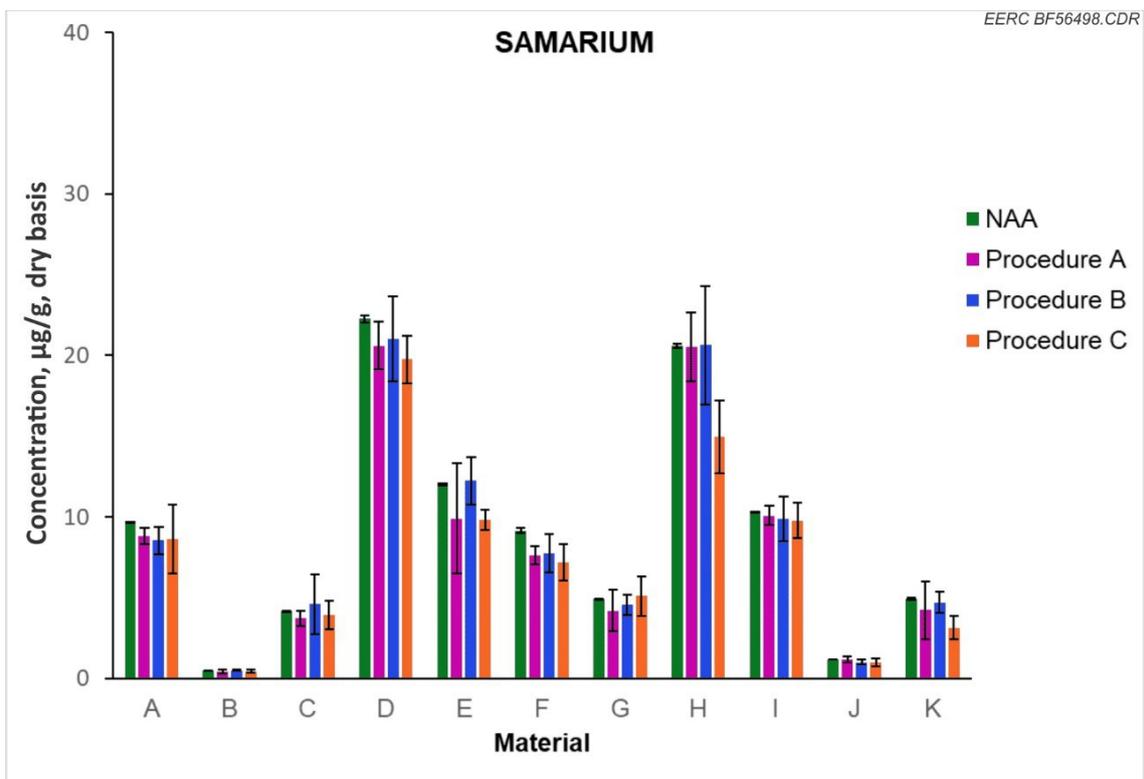


Figure 9. Mean samarium concentrations reported by the four RRIS methods.

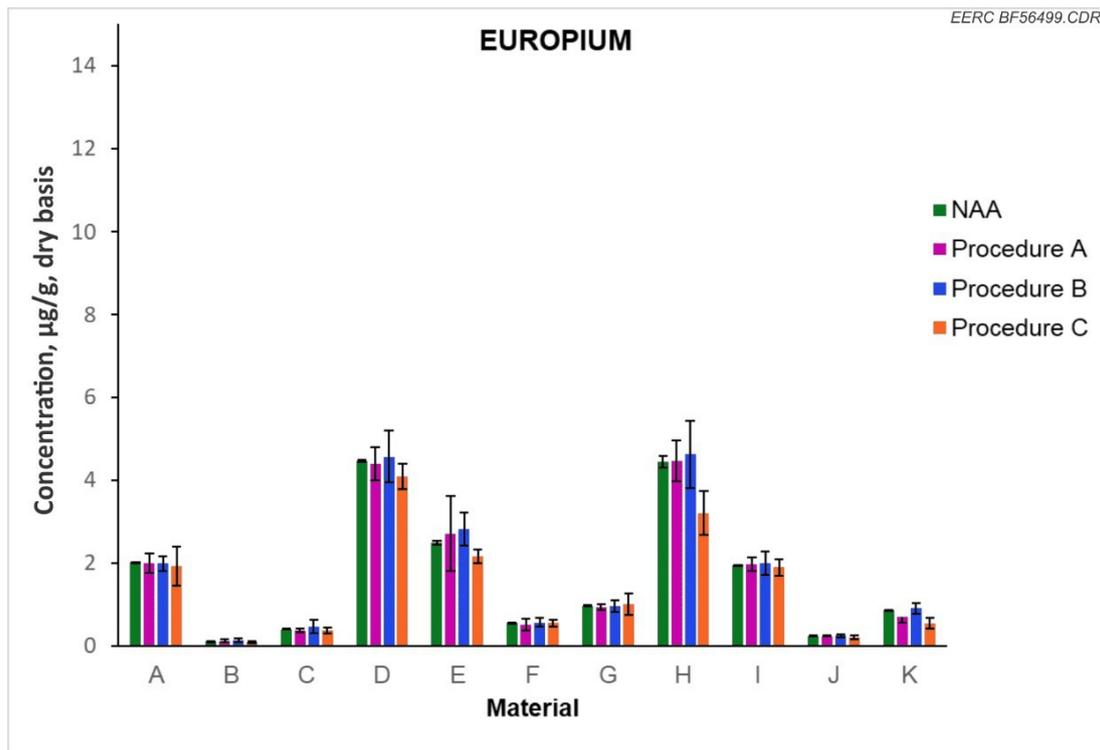


Figure 10. Mean europium concentrations reported by the four RRIS methods.

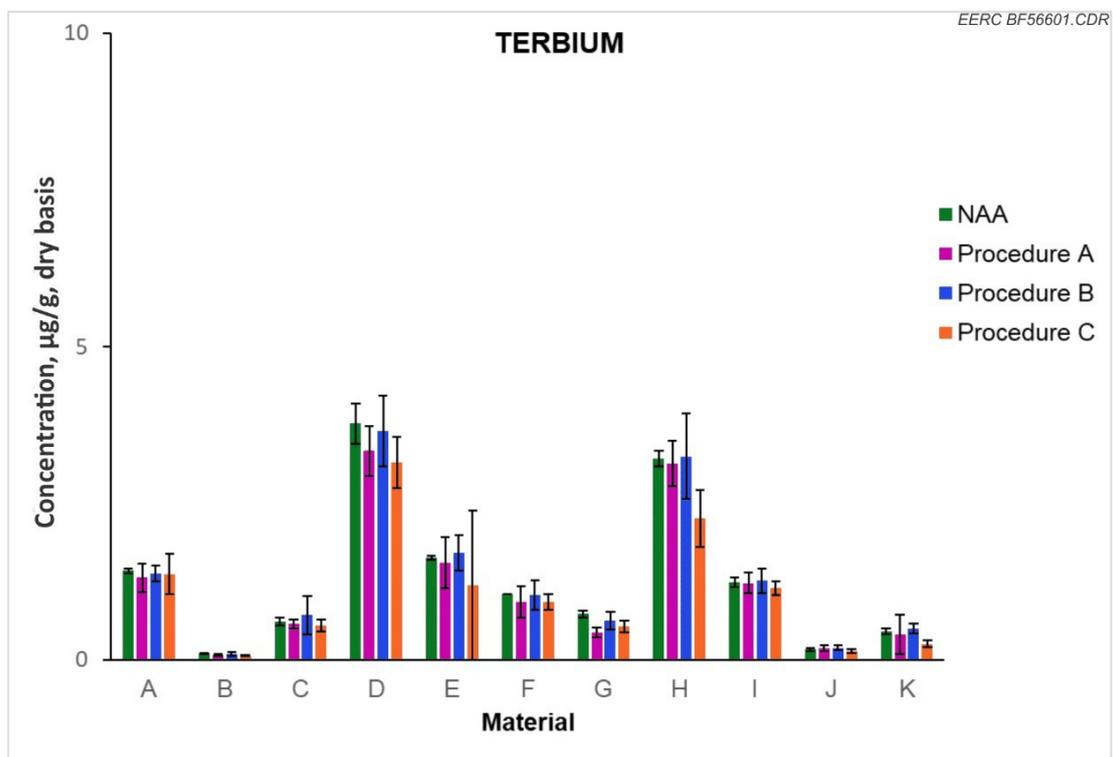


Figure 11. Mean terbium concentrations reported by the four RRIS methods.

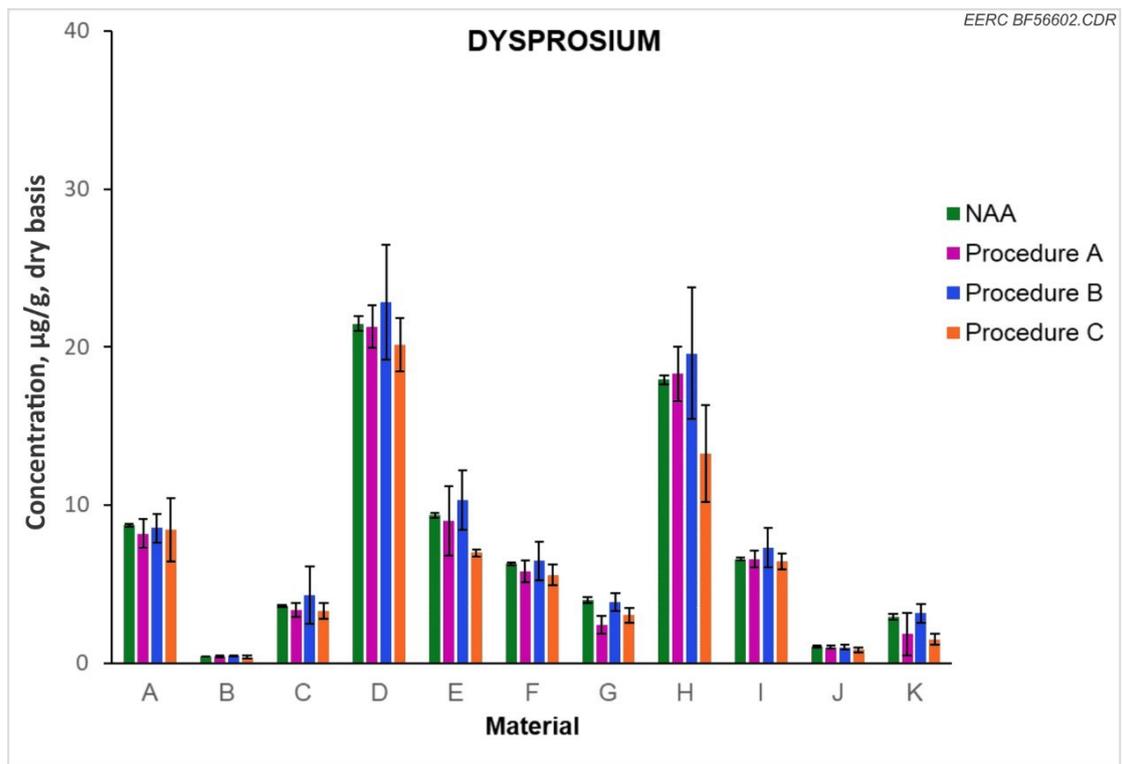


Figure 12. Mean dysprosium concentrations reported by the four RRIS methods.

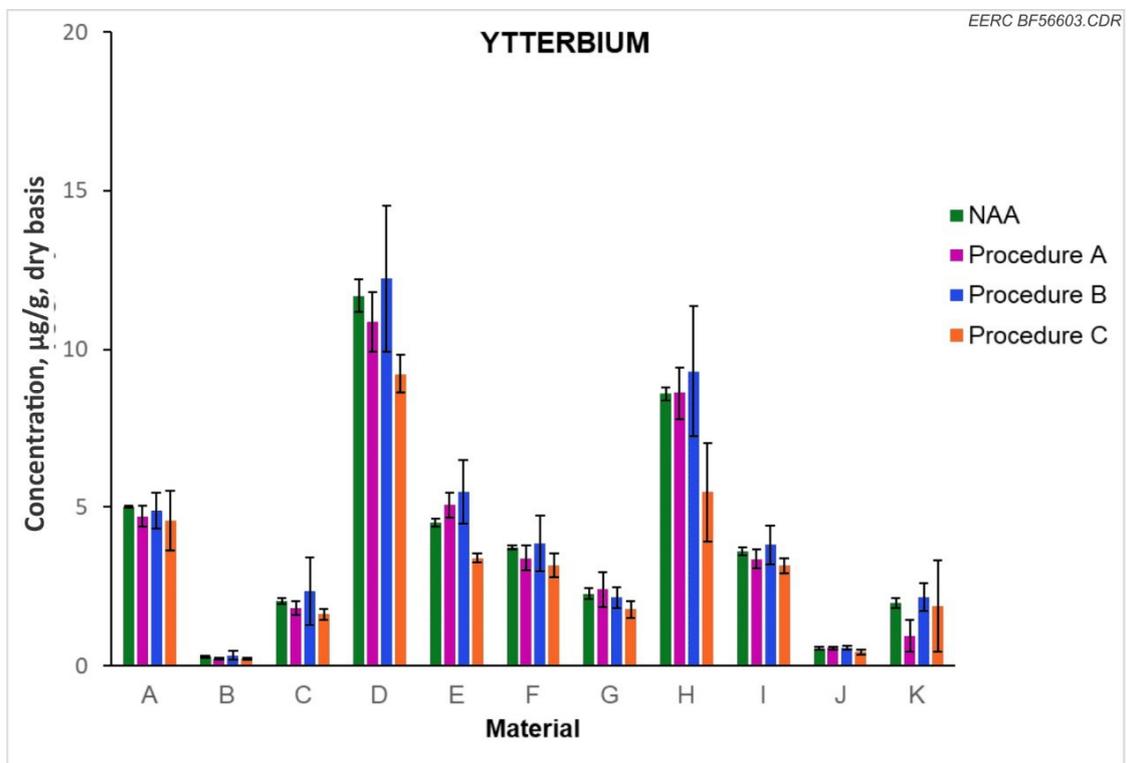


Figure 13. Mean ytterbium concentrations reported by the four RRIS methods.

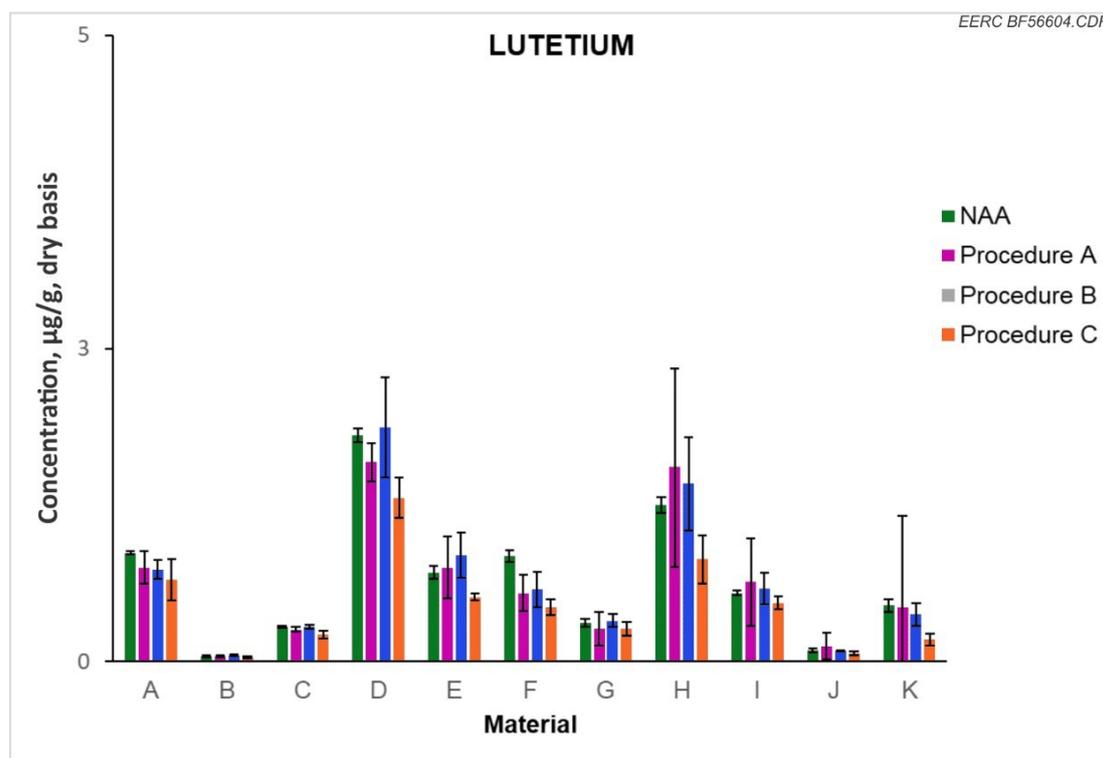


Figure 14. Mean lutetium concentrations reported by the four RRIS methods.

The materials that showed the greatest RSDs for reproducibility appear to be Material B (bituminous coal) and Material K (mine waste material), with RSD values > 35% for one or the other of Procedures A and B. Several other materials were close to 30% RSD with respect to reproducibility. Again, the higher RSD of Material B could be explained by the low concentrations of all elements found in that material. Although Material K had much higher concentrations of REEs, that particular matrix was possibly more challenging to analyze for the three methods.

Table 7. Calculated difference from NAA reference method (%); shaded cells indicate results within ±15% of the reference method.

Material	Sc	La	Ce	Nd	Sm	Eu	Tb	Dy	Yb	Lu
A	4.5%	-5.7%	-5.6%	0.3%	-8.7%	-0.8%	-7.8%	-5.9%	-6.0%	-13.9%
B	52.3%	-4.1%	-18.3%	3.0%	-14.1%	13.4%	-25.9%	0.8%	-17.4%	-5.9%
C	6.8%	-6.1%	-6.7%	-11.1%	-10.6%	-5.9%	-5.3%	-6.8%	-11.1%	-8.0%
D	2.6%	-1.7%	-2.7%	1.0%	-7.4%	-1.6%	-11.7%	-0.9%	-7.0%	-11.8%
E	40.4%	-12.3%	-5.5%	-6.8%	-17.4%	9.2%	-4.9%	-3.9%	12.0%	5.5%
F	35.1%	-5.7%	-5.2%	-6.9%	-16.9%	-7.2%	-11.2%	-7.3%	-8.7%	-35.0%
G	-6.1%	-6.7%	-0.9%	-6.6%	-14.3%	-3.0%	-39.8%	-39.6%	5.8%	-15.1%
H	5.7%	-0.6%	2.9%	4.3%	-0.5%	0.7%	-2.6%	2.1%	0.4%	24.3%
I	9.1%	-1.9%	-5.8%	3.9%	-1.8%	1.3%	-0.6%	0.2%	-6.9%	16.0%
J	6.4%	-6.7%	-3.9%	-1.0%	0.6%	1.4%	10.8%	-1.6%	2.9%	44.8%
K	-8.5%	-17.5%	-22.5%	-18.5%	-14.4%	-17.3%	-9.1%	-37.5%	-52.0%	-3.4%

Table 7. Cont.

Material	Sc	La	Ce	Nd	Sm	Eu	Tb	Dy	Yb	Lu
A	41.1%	−4.8%	−7.3%	5.4%	−11.5%	−1.3%	−2.8%	−2.1%	−2.6%	−15.5%
B	70.7%	13.6%	−2.5%	30.5%	−0.3%	26.2%	−10.4%	9.9%	17.0%	19.3%
C	21.8%	8.1%	8.3%	−4.2%	10.9%	14.6%	18.4%	18.8%	−8.5%	−1.2%
D	18.3%	−5.8%	−7.6%	−11.9%	−5.5%	2.4%	−3.3%	6.3%	4.6%	3.7%
E	48.0%	−1.9%	−2.1%	−8.2%	2.1%	13.5%	4.8%	10.0%	21.4%	19.7%
F	17.1%	−5.6%	−8.3%	−2.5%	−15.1%	3.6%	−1.3%	2.8%	3.6%	−31.5%
G	36.6%	−7.9%	−9.0%	−11.5%	−7.3%	−0.1%	−13.8%	−2.4%	−5.2%	6.5%
H	21.7%	−3.7%	−5.0%	−8.1%	0.1%	4.2%	1.1%	9.4%	8.5%	13.6%
I	32.9%	−5.4%	−6.1%	7.9%	−4.0%	2.6%	2.4%	11.1%	5.6%	7.0%
J	11.1%	−14.2%	−15.5%	−11.2%	−13.7%	2.2%	14.5%	−3.8%	2.2%	−0.5%
K	53.9%	−3.1%	−5.2%	3.8%	−4.5%	5.6%	11.1%	7.5%	9.9%	−16.1%
Material	Sc	La	Ce	Nd	Sm	Eu	Tb	Dy	Yb	Lu
A	32.1%	10.2%	7.9%	3.6%	−10.7%	−4.4%	−3.6%	−3.4%	−8.9%	−24.8%
B	77.7%	−0.2%	−0.5%	−0.8%	−9.1%	−6.3%	−34.6%	−6.7%	−21.8%	−13.1%
C	−22.7%	1.1%	6.1%	−14.9%	−5.4%	−6.9%	−8.3%	−9.0%	−20.8%	−22.8%
D	−24.9%	2.8%	2.0%	6.5%	−11.2%	−8.5%	−16.6%	−6.2%	−21.1%	−27.6%
E	171.1%	−0.2%	6.9%	−4.7%	−18.3%	−12.7%	−26.9%	−25.6%	−24.8%	−27.8%
F	38.9%	0.1%	−8.8%	−6.6%	−21.2%	0.9%	−11.6%	−11.6%	−15.0%	−48.6%
G	24.5%	23.4%	23.0%	29.9%	4.0%	4.3%	−26.2%	−23.5%	−21.7%	−14.9%
H	−10.1%	−13.2%	−7.5%	−10.5%	−27.5%	−27.8%	−29.6%	−26.0%	−36.2%	−34.8%
I	69.3%	9.4%	8.4%	11.0%	−4.9%	−2.4%	−7.5%	−2.5%	−12.5%	−14.4%
J	62.1%	−1.2%	0.4%	−4.9%	−15.2%	−14.1%	−16.9%	−19.6%	−20.6%	−23.8%
K	74.3%	−22.1%	−23.3%	−27.5%	−36.3%	−35.9%	−43.1%	−48.7%	−5.0%	−61.7%

3.4. Total Rare Earth Elements

The mean values reported by each of the laboratories, including all procedures except NAA, were totaled and the frequency distributions by material were calculated. The TREE results are summarized in Table 8 and plotted in Figures 15 and 16. The plots are split between TREEs < 300 ppm and TREEs > 300 ppm. Although the TREE mean value of Material F was slightly less than 300 ppm, it is grouped with the materials greater than 300 ppm because several of the values used to calculate the mean exceeded 300 ppm. The × within the box indicates the mean value, the horizontal bar within the box is the median value, the lower and upper horizontal bars outside the box are the min. and max. values, respectively, and the circles outside the box are outliers. The laboratory that was excluded from the reproducibility and repeatability calculations is included here in order to provide an overall look at all the data reported in the study.

Table 8. TREE * data distribution by material.

	Material A	Material B	Material C	Material D	Material E	Material F	Material G	Material H	Material I	Material J	Material K
	244	14.7	97.5	650	170	251	147	533	291	38.0	104
	238	19.9	118	638	398	264	143	575	280	42.5	171
	131	17.2	40.3	206	436	83.0	165	673	346	39.2	150
	287	17.8	147	776	381	321	151	629	317	39.8	153
	266	18.5	123	713	381	290	156	633	325	38.2	165
	259	29.9	137	706	379	299	190	610	308	42.7	192
	260	20.6	133	709	415	287	150	547	359	20.9	182
	280	17.3	130	690	398	286	164	665	316	39.1	185
	481	17.8	225	689	371	306	138	599	309	33.5	197
	261	18.2	133	671	335	310	160	493	267	40.6	200
	227		105	602	398	275	174	619	328	42.1	
	276		133	722	394	292		629			
	272		136	733							
n	13	10	13	13	12	12	11	12	11	11	10
Min.	131	14.7	40.3	206	170	83.0	138	493	267	20.9	104
Max.	481	29.9	225	776	436	321	190	673	359	42.7	200
Median	261	18	133	690	388	289	156	615	316	39.2	177
Mean	268	19.2	128	654	371	272	158	600	313	37.9	170
No. of Outliers	2	1	2	1	3	1	0	0	0	1	0

* TREE reported in µg/g (ppm), dry whole sample basis.

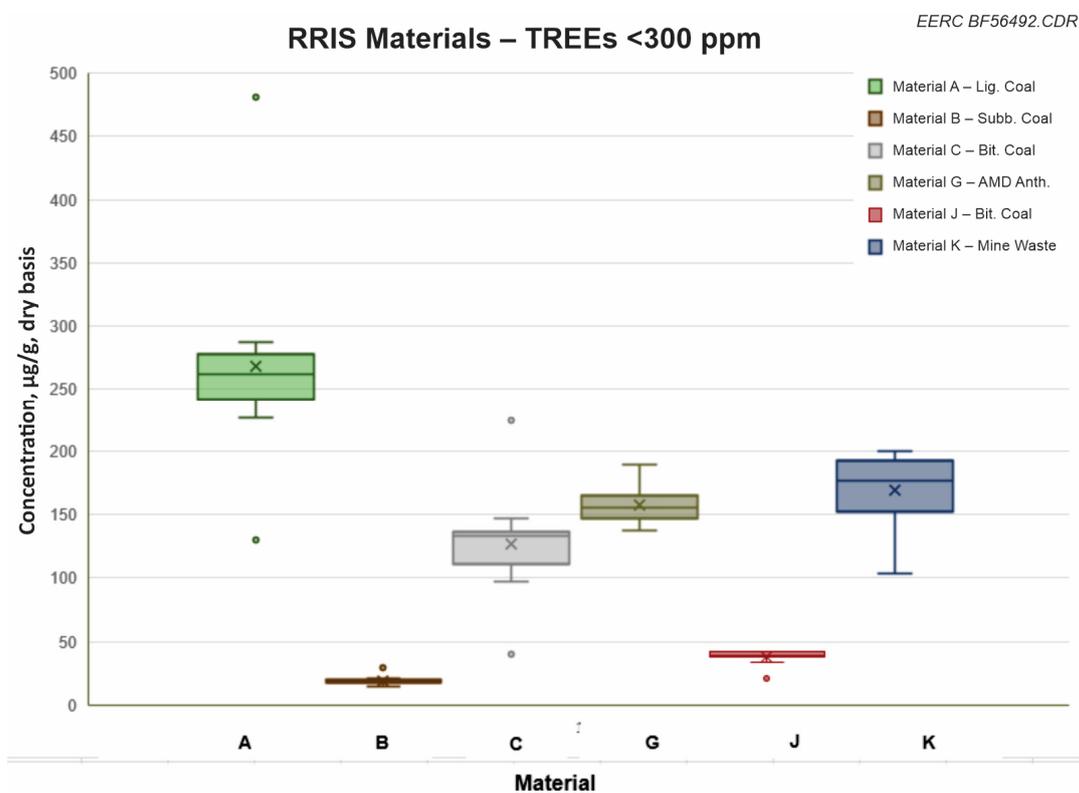


Figure 15. Distribution of TREE data < 300 ppm.

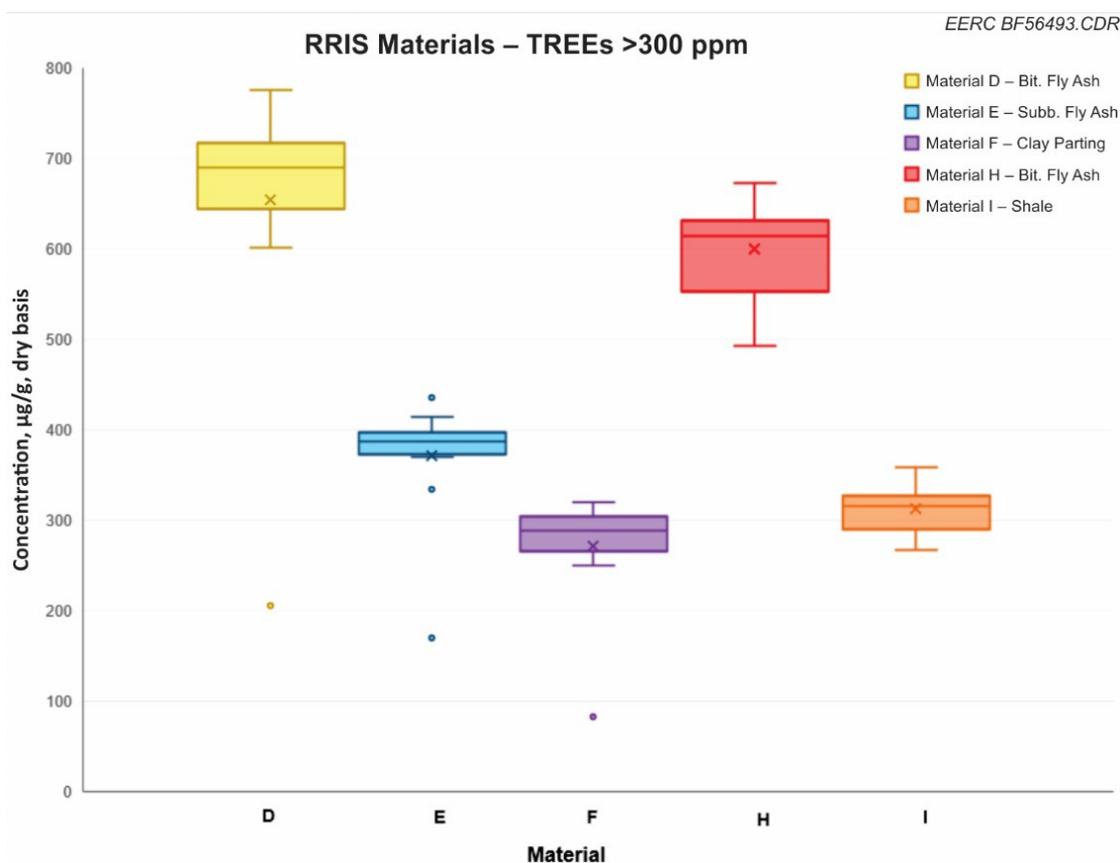


Figure 16. Distribution of TREE > 300 ppm.

These data show that the reported TREE results for several of the materials analyzed varied significantly, as can be seen from the large range between the minimum and maximum values. Of particular interest are Materials F and I, where the mean values are close to 300 ppm (272 and 313, respectively); in both cases, the minimum values were much less than 300 ppm and the maximum values were much higher. This is a significant difference when qualifying resources based solely on a >300 ppm TREE content.

4. Summary and Conclusions

Thirteen laboratories participated in an RRIS focused on analyzing REEs, a first-of-its-kind study in the United States. Analysis of REEs from eleven different materials was accomplished by the laboratories using four different procedures. The results of the RRIS suggest that NAA is the most accurate and reliable method for many of the REEs in these types of materials; however, the method is limited to determining only ten of the sixteen REEs, and is not commonly available in most laboratories. Of the other three methods in the study, Procedure A (D6357) and Procedure B (D4503) both had acceptable repeatability (within-lab) performance as well as relatively good agreement with NAA. Procedure C showed the poorest performance in these categories. The reproducibility (between-lab) results indicated a high level of variability among the labs for Procedures A and B. Scandium and lutetium were observed to have relatively high RSDs of over 60% for either Procedure A or B with respect to reproducibility of the measured quantities, whereas the RSDs for the other fourteen elements were less than 35%. The materials that showed the greatest RSDs with respect to quantification reproducibility of REEs were Material B (bituminous coal) and Material K (mine waste material), the only materials having RSD >35% for Procedures A or B. The data showed that some of the reported TREE results varied significantly based on the large range between the minimum and maximum values. Of particular interest were two materials where the mean values were close to 300 ppm

(272 and 313 ppm, respectively), which is a significant difference when qualifying resources based solely on a >300 ppm TREE content.

Although the overall between-laboratory variability was relatively higher than the within-laboratory RSDs, exceeding 13%, it is worth noting that five of the seven labs reporting data for Procedure A and three of the five labs reporting for Procedure B showed excellent performance in terms of repeatability, reproducibility, agreement with NAA, and SRM recoveries as based on AOAC international guidelines on method performance. This indicates that if strictly followed these methods are suitable for REE determination in most materials, although are subject to the overall capabilities and experience of the individual laboratories.

As of the start of this study, the ASTM D4503 method had been withdrawn as an ASTM-supported procedure in 2012. However, subsequent to this study ASTM has added this as an alternative preparation and analysis method to ASTM D6357.

In addition, the National Institute for Standards and Technology (NIST) provided four reference materials for this study which did not have certified values for many of the REEs, with the intent of using the study results after statistical review by NIST to upgrade its certificates with more certified values. This provides NIST with more CRM to provide to the public.

Author Contributions: Conceptualization, B.F. and C.N.; methodology, C.N.; formal analysis, C.N. and X.Z.; writing—original draft preparation, B.F., C.N., S.B. and X.Z.; writing—review and editing, B.F., C.N., S.B. and X.Z.; funding acquisition, B.F. and C.N. All authors have read and agreed to the published version of the manuscript.

Funding: Funding for this study was provided by the DOE National Energy Technology Laboratory under Award No. DE-FE0029007.

Data Availability Statement: Data are contained within the article.

Acknowledgments: We extend our sincere gratitude to Mary Anne Alvin, Program Manager, Critical Minerals Processing, Department of Energy, and Vito Cedro III, Program Manager, Department of Energy. Both were instrumental in guiding the project that this work came out of and graciously reviewed the manuscript. Special thanks to the laboratories that participated in the study and to ASTM Committee D05 and Subcommittee D05.29 for assistance with interpreting the data and updating the D6357 standard with methods for REE analysis.

Conflicts of Interest: The authors declare no conflict of interest.

Disclaimer: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference therein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed therein do not necessarily state or reflect those of the United States Government or any agency thereof.

Appendix A. Round-Robin Interlaboratory Study Instructions

Rare-Earth Element Round-Robin Interlaboratory Study

The user should carefully review and become familiar with the instructions, procedures, and report form prior to testing. Questions about the testing should be directed to Carolyn Nyberg at cnyberg@undeerc.org or (701) 777-5057.

Study Rationale

The purpose of this study is to evaluate the precision of methods employed by laboratories for determining rare-earth elements (REEs) in coal and related materials. The most commonly used methods are ASTM International (ASTM) D6357 and D4503 or some

variation of them. These procedures are briefly described below as Procedures A and B, respectively. For this round-robin interlaboratory study (RRIS), laboratories are requested to use one of these procedures with an option of using an alternative procedure (Procedure C) if the laboratory does not have the capabilities of either A or B. It should be noted that the procedures are written following ASTM standard formatting since this RRIS is being conducted according to ASTM E691.

Dissolution Procedure A can be performed as originally written in D6357 but also allows for modifications to reduce sample masses and acid volumes as well as allowing for hot block heating in lieu of hot plate heating. The method is described in detail in the next section following the study instructions.

Dissolution Procedure B is a modified version of D4503, which is a high-temperature fusion method using a borate fluxing agent to specifically digest samples for REE determination by inductively coupled plasma–optical emission spectroscopy (ICP–OES) and inductively coupled plasma–mass spectrometry (ICP–MS). The method is described in detail in the next section following the study instructions.

Dissolution Procedure C—An alternative procedure routinely used by the laboratory.

Basis Study Information and Materials

This study has been designed to follow the format of ASTM E691 to determine precision and bias of the different methods. Participants will receive the 11 materials listed in Table A1, some of which are controls that will be used to determine bias. All coal materials have been ground to –60 mesh and the other materials to –200 mesh. Approximate ash contents are provided to aid the analyst in determining the appropriate amount of coal to use for preparing ash for digestion.

Sample Preparation

1. Upon receipt of samples and prior to testing, all materials should be stored in a dark place. Prior to taking test portions for analysis, the material should be rolled in its container at least five turns, followed by inverting the container five times. A test portion can then be taken from the top.
2. Each material requires a moisture determination according to ASTM D3173/3173M or D7582 and ashing at either 500° or 550 °C, depending on what is specified in the procedure. This includes all materials, even those that are described as ash. Both the as-determined moisture and as-determined ash values will be entered in the report form provided. The dry ash value will be calculated.
3. After the material is ashed, three separate specimens will be weighed for digestion and analysis. A value for each of the three specimens will be reported for each element and each material.

Data Entry

4. The Excel data report form provided for this study should be used, following the instructions very closely when entering data. The report form has been formatted to guide the user to enter digest masses, digest volumes, instrument readings, and dilution factors. Calculations will be done automatically to report results on both a dry ash basis and dry whole sample basis.
5. Commas should not be entered (1,234 → 1234) (1.234 → 1.234).
6. Units should not be reported in the same cell as values.
7. Instrument readings should be entered in µg/L to four significant figures (e.g., 0.01234, 0.1234, 1.234, 12.34, 123.4, 1234).
8. For nondetect readings, ND should be entered.
9. Any deviations from the test method should be reported in the comments section. Any residue remaining in the final digest solution should be noted.

Table A1. Study Materials.

RRIS Designation	Sample Type	~Ash Content, wt%
Material A	Lignite coal	25–30
Material B	Subbituminous coal	6–8
Material C	Bituminous coal	6–8
Material D	Bituminous fly ash	98–100
Material E	Subbituminous fly ash	98–100
Material F	Clay parting	95–98
Material G	Acid mine drainage anthracite	50–55
Material H	Bituminous fly ash	90–93
Material I	Shale	90–93
Material J	Bituminous coal	8–9
Material K	Mine waste material	88–92

Submitting Data

10. The completed data report form should be submitted to cnyberg@undeerc.org.
11. Although accreditation or certification is not a requirement to participate in this study, a brief description of the laboratory's credentials and quality management system should be provided if available.
12. All calibration records (e.g., calibrants used and their assigned values) and original records for data that are reported should be retained. A review of these records may be requested if there are questions regarding reported data.
13. It should be noted that results will be coded upon receipt.

RRIS Procedures

Ashing—Weigh to the nearest 0.1 mg enough of the sample that will yield enough ash for triplicate digestions into an open 50-mL quartz or high-silica crucible. Place the crucible in a cold muffle furnace. Adjust the temperature control so that the furnace reaches a temperature of 300 °C in 1 h and then 500 °C in the second hour. Maintain the furnace temperature at 500 °C for a minimum of 2 h, stirring the sample occasionally. If following dissolution Procedure B below, increase the final ashing temperature to 550 °C. Ashing is complete when no visible evidence of carbonaceous material remains. Allow the samples to cool to room temperature under conditions that minimize the absorption of water. Grind the ash to pass a 150- μ m (No. 100) U.S.A. standard sieve in an agate mortar, then reignite at 500 °C for 1 h. If following dissolution Procedure B below, grind the ash to pass a 75- μ m (No. 200) U.S.A. standard sieve, then reignite at 550 °C for 1 h. Transfer the ash to a desiccator to cool, and store it until sampling for analysis. Determine the percentage of ash by analyzing under the same conditions a separate portion of the analysis sample.

NOTE—If all the ash from the ashing step is quantitatively transferred for digestion, it is not necessary to sieve and grind the ash.

Dissolution Procedure A—Weigh 0.2000–0.5000 g of the prepared ash into a 100-mL or 200-mL Teflon beaker. Add 20 mL of aqua regia and 20 mL of concentrated hydrofluoric acid to the beaker. Place the beaker on a hot plate that has been adjusted to 130–150 °C. Heat the mixture to dryness, but do not bake. After the solution has evaporated, rinse the beaker walls with deionized water and heat this solution to dryness, again being careful not to bake the sample. Remove the beaker from the hot plate, and allow it to cool to room temperature. Add 1 mL of concentrated nitric acid and 20 mL of deionized water to the beaker. Heat the contents on a hot plate at 90–100 °C until the sample is in solution. If a residue remains after 1 h of heating, it may be ignored. The trace elements are considered to be quantitatively extracted at this point (However, if a residue remains, report “Yes” in the appropriate cell of the reporting form). Remove the beaker from the hot plate and allow the solution to cool to room temperature. Quantitatively transfer the cool solution to a 100-mL volumetric flask and dilute to volume with deionized water. Procedure A can be modified by proportionately reducing the sample masses and acid volumes as well as using smaller digestion vessels and hot block heating instead of a hot plate, provided appropriate

validation is performed with suitable reference materials and results are comparable to those obtained from the above procedure. Prepare a method blank with each batch of samples to be analyzed.

Dissolution Procedure B—Weigh 0.0500–0.1000 g of the prepared ash into a platinum or graphite crucible. Weigh 0.4 g (to the nearest 0.5 mg) of the fluxing agent and add to the ash sample. Mix the ash and fluxing agent thoroughly. If using graphite crucibles, it is recommended to weigh the ash and fluxing agent in a separate vessel, mix thoroughly, and then transfer the contents to the crucible to avoid introducing graphite particles into the mixture. Place crucibles in a muffle furnace and heat to 1000–1100 °C for 20 min. Turn off furnace and allow samples to cool to room temperature. If using graphite crucibles, a small glass bead will have formed, which can be easily removed and transferred to a 100-mL glass or Teflon beaker. Place a clean PTFE-coated magnetic stirring bar in the beaker with the glass bead and add 30 mL 1 + 9 HNO₃. Place on stirring hot plate, set at 50–70 °C, and stir until glass pellet is completely dissolved. Other than traces of graphite particles from the crucible, no residue should remain. If using platinum crucibles, carefully rinse the bottom and outside of the crucible with deionized water to remove possible contamination, then place entire crucible in a clean 150- or 250-mL beaker. Place a clean PTFE-coated magnetic stirring bar in the platinum crucible and add 30 mL of 1 + 9 HNO₃. Stir until fused sample is completely dissolved. Alternatively, follow manufacturer's instructions if using automated fluxing equipment. No sample residue should remain after dissolution. Quantitatively transfer the digest solution to a 100-mL volumetric vessel and dilute to volume with deionized water. Samples will require further dilution with 1% HNO₃ prior to analysis to reduce matrix inferences from high dissolved solids. For ICP-MS analysis, 20× to 100× dilution is recommended to obtain optimal internal standard recovery and element detection. Prepare a method blank with each batch of samples to be analyzed.

Dissolution Procedure C—Alternative procedure routinely used by the laboratory for digesting samples for REE determination.

Instrumental Analysis

Digested solutions should be analyzed by either ICP-MS or ICP-OES according to the lab's standard operating procedures for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, and Sc.

Calculation and Reporting

Refer to The RRIS instructions and report form describe the calculation and reporting format.

References

1. U.S. Geological Survey. Rare Earths—Mineral Commodity Summaries 2016. Available online: https://minerals.usgs.gov/minerals/pubs/commodity/rare_earths/mcs-2016-raree.pdf (accessed on 21 January 2023).
2. Bao, Z.; Zhao, Z. Geochemistry of mineralization with exchangeable REY in the weathering crusts of granitic rocks in South China. *Ore Geol. Rev.* **2008**, *33*, 519–535. [CrossRef]
3. Chegwiddden, J.; Kingsnorth, D.J. Rare Earths—An Evaluation of Current and Future Supply. 2011. Available online: www.tremcenter.org/index/php?option=com_attachments&task=download&id=412011 (accessed on 21 January 2023).
4. Chi, R.; Tian, J. *Weathered Crust Elution-Deposited Rare Earth Ores*; Nova Science Publishers: New York, NY, USA, 2008.
5. Federal Register. Executive Order 13817, A Federal Strategy to Ensure Secure and Reliable Supplies of Critical Minerals. Available online: www.federalregister.gov/documents/2017/12/26/2017-27899/a-federal-strategy-to-ensure-secure-and-reliable-supplies-of-critical-minerals (accessed on 21 January 2023).
6. IEA. Executive Order 13953, Addressing the Threat to the Domestic Supply Chain from Reliance on Critical Minerals from Foreign Adversaries and Supporting the Domestic Mining and Processing Industries. Available online: www.iea.org/policies/15532-executive-order-13953-addressing-the-threat-to-the-domestic-supply-chain-from-reliance-on-critical-minerals-from-foreign-adversaries-and-supporting-the-domestic-mining-and-processing-industries (accessed on 21 January 2023).
7. The White House. Executive Order on America's Supply Chains: A Year of Action and Progress. Available online: <https://www.whitehouse.gov/wp-content/uploads/2022/02/Capstone-Report-Biden.pdf> (accessed on 21 January 2023).
8. National Energy Technology Laboratory. Critical Mineral Sustainability Program. Available online: www.netl.doe.gov/resource-sustainability/minerals-sustainability/program-overview/background (accessed on 21 January 2023).

9. *ASTM D6357-21b*; Test Methods for Determination of Trace Elements in Coal, Coke, & Combustion Residues from Coal Utilization Processes by Inductively Coupled Plasma Atomic Emission, Inductively Coupled Plasma Mass, & Graphite Furnace Atomic Absorption Spectrometry. ASTM International: West Conshohocken, PA, USA, 2011. Available online: www.astm.org (accessed on 21 January 2023).
10. *ASTM D4503-08*; Standard Practice for Dissolution of Solid Waste by Lithium Metaborate Fusion. ASTM International: West Conshohocken, PA, USA, 2011. Available online: www.astm.org (accessed on 21 January 2023).
11. *ASTM E691-18*; Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method. ASTM International: West Conshohocken, PA, USA, 2018. Available online: www.astm.org (accessed on 21 January 2023).
12. Kruskal, W.H.; Wallis, W.A. Use of ranks in one-criterion variance analysis. *J. Am. Stat. Assoc.* **1952**, *47*, 583–621. [[CrossRef](#)]
13. AOAC International. *AOAC Peer-Verified Methods Program—Manual on Policies and Procedures*; AOAC International: Rockville, MD, USA, 1993; 35p.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.