Analysis of Rare Earth Elements in Geologic Samples using Inductively Coupled Plasma Mass Spectrometry

US DOE Topical Report - DOE/NETL-2016/1794

Tracy Bank, Elliot Roth, Phillip Tinker, and Evan Granite

April 14, 2016

Analysis of Rare Earth Elements in Geologic Samples using Inductively Coupled Plasma Mass Spectrometry

Tracy Bank[b] Elliot Roth[a] Phillip Tinker[b] and Evan Granite[a*]

[a]U.S. Department of Energy, National Energy Technology Laboratory, 626 Cochrans Mill Rd, Pittsburgh, Pennsylvania 15236, USA

[b]AECOM, National Energy Technology Laboratory, Pittsburgh, PA, USA

[*]Correspondence to: Evan Granite (E-mail: *evan.granite@NETL.DOE.GOV* Phone: 412-386-4607)

Abstract

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is used to measure the concentrations of rare earth elements (REE) in certified standard reference materials including shale and coal. The instrument used in this study is a Perkin Elmer Nexion 300D ICP-MS. The goal of the study is to identify sample preparation and operating conditions that optimized recovery of each element of concern. Additionally, the precision and accuracy of the technique are summarized and the drawbacks and limitations of the method are outlined.

Keywords: Rare earth elements, Shale, Coal, Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

1. Introduction

Rare earth elements (REE) include the lanthanide series elements (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) plus Sc and Y. REE have many uses in electronics and clean energy systems and therefore the search for economic concentrations of REE is ongoing. Coal and coal ash are potentially economical sources of REE and many studies of REE concentrations in these materials have been reported. [1-21] Because REE occur in low concentrations in most geological material [22-24], their measurement is not trivial and it is important to optimize sample preparation and measurement methods to reduce uncertainty and maximize recovery.

Two of the most common methods used to analyze REE in geologic materials are Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Instrumental Neutron Activation Analyses (INAA). While INAA has the advantage of not requiring sample digestion prior to analysis, time for analysis is longer and detection limits are higher than those currently measured by ICP-MS.[25,26] A study comparing REE concentrations by both ICP-MS and INAA indicated that the two methods gave comparable results, except for an enrichment of Sm in INAA results.[27] Currently, measurement of REE by ICP-MS following solid sample digestion is the most commonly used analytical technique.[28] Pretreatment of samples, correction standards and other techniques such as Raman and X-ray fluorescence have also been used to measure REE in geological samples. [29-33]

Although the measurement of REE by ICP-MS is demonstrated to be accurate and reproducible, the proper preparation of materials for ICP-MS is crucial for accurate results. A comparative study of REE in geological reference materials using INAA and ICP-MS showed that ICP-MS was more accurate for light REE (La-Gd) compared to heavy REE (Tb-Lu), but determined that INAA produced results closer to literature values and suggested that sample preparation for ICP-MS was the cause.[34] For example, the analysis of REE in geologic samples digested using a 4-acid technique reported values lower than those measured by neutron activation analyses (NAA), likely due to incomplete digestion of highly insoluble mineral phases.[35, 36]

In this study we present the concentrations of REE in geologic samples following optimized sample preparation using solid fusion followed by acid digestion and measurement with ICP-MS in kinetic energy discrimination (KED) mode. We present the results of three standard reference materials including two shales and one bituminous coal. While the REE concentrations of these three materials are not all certified, consensus and informational values for many of the REE are published. The results of this study show that high accuracy and good precision can be obtained without the use of correction equations or ion-exchange pretreatment.

2. Methods and Materials

A Perkin Elmer Nexion 300D ICP-MS with universal cell technology was used for all data collected in this study. The instrument was operated under standard mode as well as using KED mode with He as the collision cell gas. All analyses were completed using 50 ppb In as an internal standard. Solid samples were prepared by mixing pulverized sample (<200 mesh) with calcined $LiBO_2$ (lithium metaborate) at a ratio that varied from 1:10 to 1:4 until optimized recoveries were determined. Prior to fusion, samples are mixed by stirring with a platinum rod in a platinum crucible. Two types of platinum crucibles, 99.95% Pt and 95% Pt/5% Au were employed to determine which material produced the best recovery of REE. The open crucibles were heated to 1100°C for five minutes in a Phoenix microwave muffle furnace (CEM). After fusion, the melt was removed from the oven and allowed to cool to a homogeneous glass. The glass was digested in 5% HNO_3 on low heat with continuous stirring. The platinum crucibles were rinsed in triplicate with 5% HNO_3 to ensure that the sample glass was completely digested and the sample was diluted to a final volume of 100 ml. These samples were further diluted between 10-100x in 2% HNO_3 before analysis to determine the optimal balance between internal standard recovery and limit of detection. For each set of fusions prepared for this study, blank samples containing only the lithium metaborate were prepared and processed identically to the samples. All data presented in this study are blank subtracted.

The effects of sample preparation prior to fusion were also studied. Samples were dried for one hour under nitrogen at 107°C and ashed for five hours under air at 550°C using a Leco Thermogravimetric Analyzer (TGA701).

Samples used in this study include the carbon-poor Brush Creek Shale from Pennsylvania (SBC-1), an oil-rich Green River Shale from Wyoming (SGR-1b), and a NIST coal standard (SRM 1632a). Of these standard reference materials, only the SGR-1b has certified values for some of the REE, however published consensus values for the other standards are available for many of the rare earth elements. Additionally, values for many REE were also compared to a certified natural water standard (T221) from the USGS Water Resources Division.

3. Results

The expected results of the standard reference materials used in this study are presented in Table 1. The results of different sample preparation and analyzing conditions are presented in Figure 1. All concentrations are presented on a whole rock, blank-subtracted basis.

Table 1. Certified and consensus values of rare earth elements in SBC-1, SGR-1b, and SRM 1632a. All concentrations in mg/kg. Values in italics are non-certified consensus or informational data.

Element	SBC-1	SGR-1b	SRM 1632a
Sc	*20*	4.6 ± 0.7	*6.3*
Y	*36.5*	*13*	*9*
La	*52.5*	20 ± 1.8	*15*
Ce	*108.2*	36 ± 4	*30*
Pr	*12.6*		*3.15*
Nd	*49.2*	16 ± 1.7	*12*
Sm	*9.62*	2.7 ± 0.3	*2.4*
Eu	*1.98*	0.56 ± 0.09	*0.52*
Gd	*8.54*	*2*	*2.6*
Tb	*1.23*		*0.311*
Dy	*7.1*	*1.9*	*2.06*
Ho	*1.36*	*0.4*	*0.36*
Er	*3.79*	*1.1*	*0.91*
Tm	*0.56*	*0.17*	*0.39*
Yb	*3.64*	*0.94*	*1.08*
Lu	0.54		0.17

<u>Effects of sample preparation</u>. For samples with low total organic carbon (TOC) content, including SBC-1, the effects on the recovery of REE of drying and ashing the sample prior to fusion is negligible. The SRM 1632a coal sample with a certified 64.6% carbon concentration does not fuse completely without ashing (results not shown). SGR-1b showed a statistically insignificant improvement in recovery when dried and ashed prior to fusion.

In this study the optimal ratio of fusion flux to sample was determined to be 1:8 using 0.05 g sample and 0.400 g $LiBO_2$. This ratio was determined based on the homogeneity of the glass fused, ease of digest of the glass in 5% HNO_3 and on the presence of any undissolved flux in the acid digest.

The crucible material played a significant role in the ease of fusion of the samples used in this study. The samples fused in the 99.95% Pt crucible generated a more homogeneous glass that was much easier to digest in 5% HNO_3 compared to the samples fused in the 95% Pt/5% Au alloy crucibles (Figure 1a). Glasses that formed in the Pt/Au crucible were more likely to form several small, discrete glass beads that were slower to digest in acid and more likely to be lost during sample preparation. The differences in fusion are likely caused by the differences in wettability of the two crucible materials. Pt/Au alloy is a non-wetting surface that doesn't allow for as much adhesion of the glass to the crucible, thereby creating numerous smaller glass beads which can be lost in digestion.

Figure 1a. Effects of crucible material on recovery of REE for SRM 1632a. Red line represents digestion in 95% Pt/ 5% Au alloy. Black line represents digestion in 99.95% Pt.
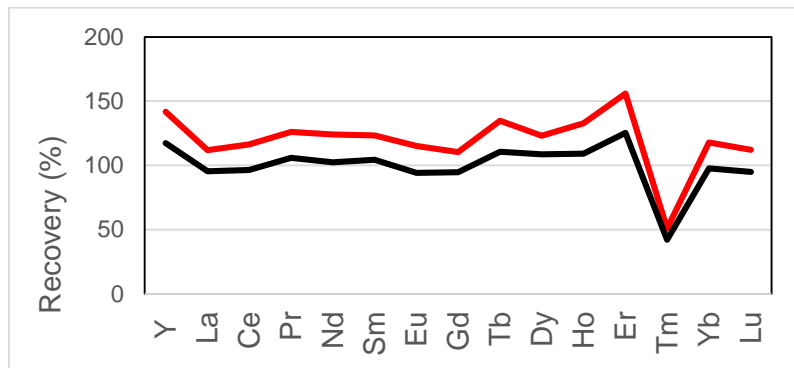
All samples were analyzed in both ICP-MS standard operating mode and optimized with KED mode. KED mode allows the user to supply a non-reactive gas (He) that physically interacts with the ionized sample. He physically collides with the largest and most abundant ions in the sample, thereby lowering their kinetic energy and decreasing their likelihood of reaching the detector. KED mode allows the user to analyze samples with higher total dissolved solids without large dilution factors and therefore lowers the detection limit for many elements. The results of using KED mode to detect REE in both the SRM 1632a and SBC-1 samples are shown in Figure 1b.

Figure 1b. Effects of KED mode (black line) compared to standard mode (red line) for recoveries of REE from SRM 1632a (solid line) and SBC-1 (dashed line).
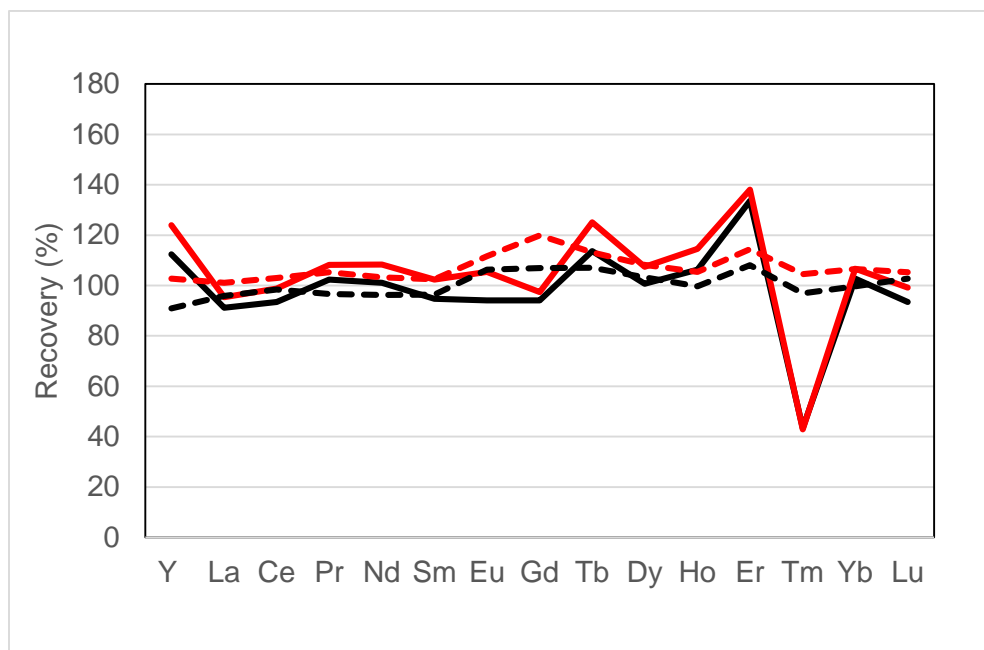
The distinctly low recovery of Tm in the SRM 1632a sample may be attributed to inaccurate published consensus values. The consensus value of 390 μg/kg is based on just 2 measured values, neither of which used ICP-MS. Additionally, the consensus value of SRM 1632 coal, which preceded SRM 1632a, is 300 μg/kg with one reported value of just 110 μg/kg and a large standard deviation.[37] Accurate recoveries of similar

and lower concentrations of Tm from SBC-1 and SGR-1b indicate that the methods used in this study should also be accurate for recovery of Tm in SRM 1632a (Fig. 1c).

Figure 1c. Expected concentrations (bold) in μg/kg and measured recoveries (%) of Tm in 1632a, SBC-1, and SGR-1b.
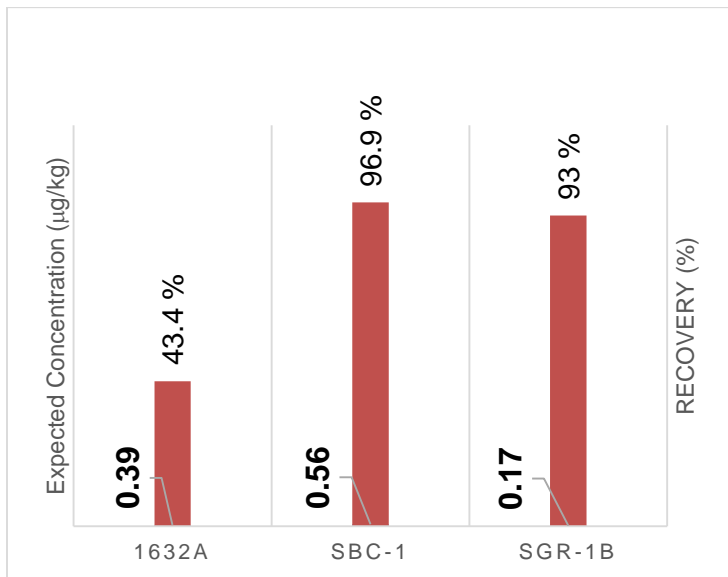
The optimal conditions that produced the highest recoveries of REE in three standard reference materials are presented in Table 2. These conditions are optimal for the silicate-based material that dominates the composition of these solids, but may not be suitable for different, non-silicate materials.

Table 2. Optimal conditions for REE measurement determined in this study.

Sample Preparation	Drying and Ashing of samples containing >25 wt% TOC
Sample/ Fusion Flux	0.05g sample / 0.4 g lithium metaborate
Crucible Material	99.95 % Pt
ICP-MS measurement mode	KED

4. Drawbacks and Limitations

The lithium metaborate fusion and acid digestion technique for analyzing REE in silicate-based geologic samples is not without limitations and drawbacks. For example, analysis of lithium or boron in the sample is precluded by the high concentration of these elements in the fusion flux. Scandium also is poorly recovered from lithium metaborate fused solids due to numerous interferences; BO_2 from the metaborate is likely the largest interference at 45 amu. Additionally, limits of detection are typically in the low μg/kg range for the rare earth elements and these values may be too high to quantitatively determine some of the heavier REE in REE-poor silicate rocks (Table 3).

Table 3. Typical limits of detection (LOD) of REE using KED mode ICP-MS. Results are the averages of 30 separate analyses. Concentrations are in mg/kg.

Element	LOD (mg/kg)
Sc	4
Y	0.3
La	0.06
Ce	0.05
Pr	0.05
Nd	0.1
Sm	0.04
Eu	0.02
Gd	0.04
Tb	0.007
Dy	0.05
Ho	0.007
Er	0.03
Tm	0.007
Yb	0.01
Lu	0.007

While issues of oxide interferences were not detected in these samples, literature has reported that high oxide concentrations can cause erroneously high measured values for REE [38]. Specifically, high Ba values can create BaO interferences that overlap with the only isotopes for ^{151}Eu and ^{153}Eu. Methods optimized in this study would not eliminate these errors in samples with very high (i.e., greater than 10-100 mg/kg) barium concentrations.

A secondary issue is that the fusion crucible must be cleaned in between use to ensure that no carryover of sample occurs. Adhesion to or reaction with the walls of the crucible could cause contamination of the sample. Cleaning the crucibles in between use can minimize these issues. In this study crucibles were cleaned in warm water with an acid cleaner\detergent (Citranox), rinsed in triplicate with tap water, rinsed in triplicate with DI water, and then dried in a muffle furnace for 30 minutes at 107 °C. Additionally, the chemistry of the platinum itself can react with the sample and lead to minor leaching of trace metals into the sample. In particular, Pt often contains trace Rh that can leach out into the sample. For this reason Rh should not be used as an internal standard in ICP-MS analyses.

5. Conclusions

In this study the methods of sample preparation and analysis by ICP-MS were optimized to maximize the recovery of rare earth elements in standard reference materials of geological nature. The results obtained are comparable to a recently published study of REE from coal ash using ICP-MS. Kashiwakura and others obtained calculated recoveries of 92%-118% for certified values of La, Ce, and Eu, and 72%-133% for informational values of Sc, Sm, Tb, Yb, Lu, Y, Pr, Nd, Gd, and Dy in a fly ash standard reference material.[39] These results show that error of ± 10% can be expected even after careful optimization of sample preparation and analysis. Extreme care in sample preparation, equipment calibration, and reducing contamination from lab equipment should be emphasized.

Lastly, certified REE concentrations for natural (non-ore material) geological samples are rare. Consensus and informational values for these standard reference materials are commonly used as quality checks of data produced. Historical data for decades-old standard reference materials collected by techniques that have been replaced by newer technologies should not be expected to agree perfectly. The scientific community would benefit from the production of more geostandards certified in rare earth elements.

The possible recovery of rare earth and other critical elements from abundant coal and by-products is an exciting new research area, representing a dramatic paradigm shift for coal.   The rare earth contents of coals and by-products are required in order to determine the most promising potential feed materials for extraction processes.

6. 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 herein 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 herein do not necessarily state or reflect those of the United States Government or any agency thereof."

8. **Literature Cited**

1. Crowley, S.S., R.W. Stanton, and T.A. Ryer, *The effects of volcanic ash on the maceral and chemical composition of the C coal bed, Emery Coal Field, Utah.* Organic Geochemistry, 1989. **14**(3): p. 315-331.

2. Cutruneo, C.M., et al., *A mineralogical and geochemical study of three Brazilian coal cleaning rejects: demonstration of electron beam applications.* International Journal of Coal Geology, 2014. **130**: p. 33-52.

3. Dai, S., et al., *Mineralogy and geochemistry of boehmite-rich coals: New insights from the Haerwusu Surface Mine, Jungar Coalfield, Inner Mongolia, China.* International Journal of Coal Geology, 2008. **74**(3–4): p. 185-202.

4. Dai, S., et al., *Revisiting the late Permian coal from the Huayingshan, Sichuan, southwestern China: Enrichment and occurrence modes of minerals and trace elements.* International Journal of Coal Geology, 2014. **122**(0): p. 110-128.

5. Dai, S., et al., *Mineralogy and geochemistry of the No. 6 Coal (Pennsylvanian) in the Junger Coalfield, Ordos Basin, China.* International Journal of Coal Geology, 2006. **66**(4): p. 253-270.

6. Dai, S., et al., *Petrology, mineralogy, and chemistry of size-fractioned fly ash from the Jungar power plant, Inner Mongolia, China, with emphasis on the distribution of rare earth elements.* Energy and Fuels, 2014. **28**(2): p. 1502-1514.

7. Dai, S., et al., *Abundances and distribution of minerals and elements in high-alumina coal fly ash from the Jungar Power Plant, Inner Mongolia, China.* International Journal of Coal Geology, 2010. **81**(4): p. 320-332.

8. Eskenazy, G.M., *Rare earth elements and yttrium in lithotypes of Bulgarian coals.* Organic Geochemistry, 1987. **11**(2): p. 83-89.

9. Eskenazy, G.M., *Zirconium and hafnium in Bulgarian coals.* Fuel, 1987. **66**(12): p. 1652-1657.

10. Eskenazy, G.M., *Rare earth elements in a sampled coal from the Pirin deposit, Bulgaria.* International Journal of Coal Geology, 1987. **7**(3): p. 301-314.

11. Eskenazy, G.M., *Aspects of the geochemistry of rare earth elements in coal: an experimental approach.* International Journal of Coal Geology, 1999. **38**(3–4): p. 285-295.

12. Eskenazy, G.M., E.I. Mincheva, and D.P. Rousseva, *Trace-Elements in Lignite Lithotypes from the Elhovo Coal Basin.* Dokladi Na Bolgarskata Akademiya Na Naukite, 1986. **39**(10): p. 99-101.

13. Hower, J.C., S. Dai, and V.V. Seredin, *A Note on the Occurrence of Yttrium and Rare Earth Elements in Coal Combustion Products.* Coal Combustion and Gasification Products, 2013. **5**: p. 39-47.

14. Hower, J.C., et al., *Location of Cerium in Coal-Combustion Fly Ashes: Implications for Recovery of Lanthanides.* Coal Combustion and Gasification Products, 2013. **5**: p. 73-78.

15. Hower, J.C., L.F. Ruppert, and C.F. Eble, *Lanthanide, yttrium, and zirconium anomalies in the Fire Clay coal bed, Eastern Kentucky.* International Journal of Coal Geology, 1999. **39**(1-3): p. 141-153.

16. Pazand, K., *Geochemical properties of rare earth elements (REE) in coals of Abyek coalfield, North Iran.* Arabian Journal of Geosciences, 2014: p. 1-8.

17. Qi, H., R. Hu, and Q. Zhang, *REE geochemistry of the Cretaceous lignite from Wulantuga germanium deposit, Inner Mongolia, northeastern China.* International journal of coal geology, 2007. **71**(2): p. 329-344.

18. Wang, X., et al., *Rare earth element geochemistry and fractionation in Jurassic coal from Dongsheng–Shenmu area, Ordos Basin.* Fuel, 2014. **136**(0): p. 233-239.

19. Yossifova, M.G., *Petrography, mineralogy and geochemistry of Balkan coals and their waste products.* International Journal of Coal Geology, 2014. **122**(0): p. 1-20.

20. Zhao, C., et al., *Rare earth elements in No. 2 coal of Huangling mine, Huanglong coalfield, China.* Energy, Exploration & Exploitation, 2012. **30**(5): p. 803-818.

21.   Eskenazy, G., *Rare-earth elements in some coal basins of Bulgaria.* Geologica Balcanica, 1978. **8**(2): p. 81-88.

22.   Gromet, L.P., et al., *The "North American shale composite": Its compilation, major and trace element characteristics.* Geochimica et Cosmochimica Acta, 1984. **48**(12): p. 2469-2482.

23.   Haskin, M.A. and L.A. Haskin, *Rare earths in European shales: a redetermination.* Science, 1966. **154**(3748): p. 507-509.

24.   Taylor, S.R. and S.M. McLennan, *The continental crust: its composition and evolution.* 1985.

25.   Golighty, D. and F.O. Simon, *Methods for sampling and inorganic analysis of coal.* 1989.

26.   Palmer, C. and P. Baedecker, *The determination of 41 elements in whole coal by instrumental neutron activation analysis.* Methods for sampling and inorganic analysis of coal: US Geological Survey Bulletin, 1989. **1823**: p. 27-34.

27.   Cruse, A.M., *Rare-earth element behavior in phosphates and organic-rich host shales: an example from the Upper Carboniferous of Midcontinent North America.* 2000.

28.   Potts, P.J., P.C. Webb, and M. Thompson, *Bias in the Determination of Zr, Y and Rare Earth Element Concentrations in Selected Silicate Rocks by ICP-MS when Using Some Routine Acid Dissolution Procedures: Evidence from the GeoPT Proficiency Testing Programme.* Geostandards and Geoanalytical Research, 2015. **39**(3): p. 315-327.

29.   Lee, K.-H., et al., *Determination of lanthanoids and yttrium in JGb2 and JR3 by inductively coupled plasma-mass spectrometry after cation-exchange pretreatment.* Geochemical Journal, 2000. **34**(5): p. 383-393.

30.   Makreski, P., et al., *Simple and efficient method for detection of traces of rare earth elements in minerals by raman spectroscopy instrumentation.* Macedonian Journal of Chemistry and Chemical Engineering, 2011. **30**(2): p. 241-250.

31.   Raut, N.M., et al., *Determination of lanthanides in rock samples by inductively coupled plasma mass spectrometry using thorium as oxide and hydroxide correction standard.* Spectrochimica Acta Part B: Atomic Spectroscopy, 2003. **58**(5): p. 809-822.

32.   Zawisza, B., et al., *Determination of rare earth elements by spectroscopic techniques: a review.* Journal of Analytical Atomic Spectrometry, 2011. **26**(12): p. 2373-2390.

33.   Bayon, G., et al., *Determination of rare earth elements, Sc, Y, Zr, Ba, Hf and Th in geological samples by ICP-MS after Tm addition and alkaline fusion.* Geostandards and Geoanalytical Research, 2009. **33**(1): p. 51-62.

34.   Doi Kin, F., et al., *Determination of rare earth elements in geological reference materials: A comparative study by INAA and ICP-MS.* Geostandards Newsletter, 1999. **23**(1): p. 47-58.

35.   Totland, M., I. Jarvis, and K.E. Jarvis, *An assessment of dissolution techniques for the analysis of geological samples by plasma spectrometry.* Chemical Geology, 1992. **95**(1): p. 35-62.

36.   Tsai, C. and S. Yeh, *Determination of rare earth elements in Taiwan monazite by chemical neutron activation analysis.* Journal of radioanalytical and nuclear chemistry, 1997. **216**(2): p. 241-245.

37.   Gladney, E.S., *Compilation of elemental concentration data for NBS clinical, biological, geological, and environmental standard reference materials.* 1987.

38.   Mysovskaya, I.N., E.V. Smirnova, and V.I. Lozhkin, *Interferences of polyatomic and doubly charged ions in the multielement analysis of geological samples by inductively coupled plasma mass spectrometry and their minimization on a high-resolution mass spectrometer.* Journal of Analytical Chemistry, 2013. **68**(14): p. 1217-1226.

39.   Kashiwakura, S., et al., *Dissolution of Rare Earth Elements from Coal Fly Ash Particles in a Dilute H_2SO_4 Solvent.* Open Journal of Physical Chemistry, 2013. **3**(2).