

## Direct Determination of Rare Earth Elements by ICP-MS after Fluoride Fusion –Application to Bauxite

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### ABSTRACT

Rare earth elements (REEs) have emerged as an economically important group of metals owing to their application in several key technologies. Bauxite, an aluminium ore is under consideration as an alternative source of REEs in several countries. It is extremely difficult to achieve complete sample decomposition of bauxite for chemical analysis owing to its refractory nature. In the present work, a fluoride fusion method has been applied for sample dissolution prior to ICP-MS determination of rare earth elements in bauxite. The analytical results obtained for some selected bauxite samples are presented in this paper. To check the accuracy of results obtained, the samples were also analysed by an alternate ICP-OES method after sodium peroxide fusion and the results obtained compared. For further validation, a bauxite certified reference material (BCS-CRM No.395) was analysed by both methods and the results presented in this paper. The fluoride fusion method is effective in achieving complete dissolution of bauxite samples as evidenced from the results obtained.

**Keywords:** Bauxite, ICP-MS, Rare-earth elements, Fluoride fusion.

### INTRODUCTION

The rare earth elements (REEs) contribute greatly to research in geosciences since the knowledge of their distribution in a wide range of rock types is necessary for many geochemical and petro-genetic investigations<sup>1</sup>. They have also emerged as an important group of elements owing to their use in a wide gamut of emerging technologies like smart phones, electric cars and wind turbines<sup>2</sup>. Demand for REEs is increasing, particularly for use in green

energy technologies. Recycling is considered as an option and may contribute to meeting future demand but the separation of individual REEs from recycled materials is very challenging with only one per cent of REEs currently produced obtained from recycling of end-of-life products.

Main source of REEs is the mineral “Bastnasite”, which occurs largely in China<sup>2</sup>. Alternative resources of REEs have been identified in a variety of other environments such as alluvial or beach placer deposits, bauxites and ore tailings. There is increasing pressure to identify alternative sources of these economically important metals in many countries owing to supply concerns<sup>3</sup>. One such source under consideration is bauxite. Bauxite is a sedimentary rock enriched in aluminum hydroxide minerals and constitutes the major raw material in the production of aluminum by the Bayer process. Research into the potential of bauxites as a source of REEs, Sc and Y has been undertaken by many researchers over the past forty years<sup>4</sup>. REEs have been identified as being particularly enriched in “Karst-bauxites” which are mainly located in Europe, Jamaica, Russia and China. “Red mud” generated as a waste product from the processing of these bauxites to alumina through the Bayer process contains on average 900 ppm REEs compared with typical values of <100 ppm to ~500 ppm REEs in the bauxites<sup>5</sup>. In view of the above, there exists a need for accurate and precise chemical analysis of bauxite samples for determination of their REE contents.

Bauxite samples are refractory and highly resistant to open acid decomposition. Hence, fusion procedures are employed to bring about complete decomposition of bauxite. X-ray fluorescence spectrometry (XRF) after fusion of sample is an established technique for the determination of major and minor constituents in bauxite<sup>6</sup>. An instrumental neutron activation analysis method has been reported for determination of twelve rare earth elements in red and white bauxites<sup>7</sup>.

Rare earth elements are widely analyzed using the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). ICP-OES technique has occupied an invaluable position in the modern analytical laboratory due to excellent sensitivity, good specificity, precision and accuracy, wide dynamic range, and simple operation<sup>8</sup>. But, because of the low concentrations, REEs in bauxite cannot be determined directly by ICP-OES<sup>9-10</sup>. Aluminum in high concentrations (>1000 µg/ mL) interferes strongly in the determination of trace amounts of several elements when ICP-OES is used. The high iron content also leads to spectral interferences. It is therefore necessary to separate the REEs from the bulk aluminium-iron matrix and pre-concentrate these elements by using a suitable technique before final measurement<sup>11</sup>. On the contrary, ICP-MS determinations require no additional separation and pre-concentration steps owing to the superior sensitivity.

In the present paper, a fluoride fusion method has been applied for the direct, accurate and precise determination of REEs and yttrium in iron-aluminum rich matrices such as bauxites. The sample solutions were directly analysed for these elements by inductively coupled plasma mass spectrometry (ICP-MS), after complete dissolution of the samples by fusion with a mixture of sodium fluoride- potassium bi-fluoride salts (KHF<sub>2</sub>-NaF) in 3:1 weight ratio, without using any separation or pre-concentration step.

## MATERIALS AND METHODS

### Instrumentation

An ICP-MS (Platform XS, Micromass Ltd., U.K) was used for the determinations. The instrumental parameters and operating conditions of ICP-MS is listed in Table-1.

**Table- 1 Instrumental Parameters of ICP-MS**

Analyser	
Cone lens voltage	- 390 V
Hexapole Exit Lens voltage	- 380 V
Hexapole bias	0.0 V
Detector	
Photo multiplier voltage	450 V
Pressures	
Analyser vacuum	10 <sup>-5</sup> mbar
Torch	
Forward Power	1250 W
Gas	
Plasma-Cool gas	13.5 L min <sup>-1</sup>
Plasma-Intermediate gas	1.3 L min <sup>-1</sup>
Plasma-Nebuliser gas	1.0 L min <sup>-1</sup>
Hexapole gas- Helium	8.0 mL min <sup>-1</sup>
Hexapole gas –Hydrogen	4.0 mL min <sup>-1</sup>
Solution uptake rate(pumped)	1mL min <sup>-1</sup>
Spray chamber temperature	3-4 <sup>o</sup> C
Sampler cone	Ni-Cu, 1.1mm orifice diameter
Skimmer cone	Ni, 0.7 mm orifice diameter
Acquisition mode	Peak hopping (SIR)
Dwell time	200 ms

### Reagents and Standards

All reagents used were of analytical grade. All solutions were made using ultrapure (resistivity 18 M $\Omega$  cm<sup>-1</sup>) water. Analytical grade mineral acids were procured and purified further prior to use by sub-boiling distillation. Traceable elemental standard stock solutions (1mg/mL) were procured from Alfa Aeser Pvt. Ltd. (Johnson Matthey) for all elements determined. Mixed multi-element working standard solutions were prepared from the above stock solutions by appropriate dilution. Solutions of SY-2 and SY-3 CRM (supplied by Canadian certified reference materials project), prepared in similar manner as sample solutions, were also used for calibration of REEs and yttrium by ICP-MS.

### **Analytical Procedure**

A 0.1 g sample portion was accurately weighed and mixed with 2 g flux (a homogenous mixture of  $\text{KHF}_2$  and NaF salts in 3:1 weight ratio) in a platinum crucible and fused over a burner till the melt was red hot and clear. The crucible was cooled; 5 mL of 18 N sulphuric acid was added and heated on a hot plate (for removal of fluoride) till the evolution of dense white fumes ceased. After cooling, the contents of the crucible were dissolved in 5 mL of 16M nitric acid and ultrapure water, and transferred into a 250 mL beaker. The solution was boiled until clear, transferred into a 100 mL volumetric flask and made up to volume using ultrapure water. This solution was used for determination of major and minor constituents by ICP-OES and REEs determination by ICP-MS after appropriate dilution. Procedural blank solutions were also prepared concurrently following the same procedure.

### **RESULTS AND DISCUSSION**

Five bauxite samples originating from Madhya Pradesh state in India with varying iron and aluminum contents were selected for the present study.

#### **Studies on Sample Dissolution**

Dissolution of bauxite samples using acids is not successful as it often results in incomplete decomposition. Literature shows that quantitative recoveries of REEs are not obtainable using acid leaching methods<sup>12</sup>. Hence, fusion procedures are employed for bauxite decomposition. Fusion digestion methods have many advantages over the conventional open acid digestion methods as they avoid the use of hazardous acids and result in complete sample decomposition including refractory mineral phases like zircon. Fusion methods are relatively faster as samples can be processed batch wise without deployment of any specialized equipment. Different fluxes have been reported for bauxite decomposition. Mukhedar and Kulkarni<sup>13</sup> reported that sodium peroxide sintering is preferable to sodium carbonate as it is faster for complete decomposition of bauxite. Complete dissolution of bauxite by alkali fusion with a mixture of sodium carbonate and sodium tetra borate decahydrate prior to ICP-MS determination has also been reported<sup>14</sup>. Although lithium meta-borate ( $\text{LiBO}_2$ ) fusion is a powerful decomposition technique for geological materials by ICP-MS, this method necessitates deployment of a muffle furnace owing to the high fusion temperature ( $\sim 1050^\circ\text{C}$ ) involved.

The authors attempted sodium carbonate fusion first which however did not result in complete sample decomposition. Sodium peroxide fusion resulted in effective sample decomposition but since the fusion is carried out in nickel crucibles, the resulting solution has high levels of total dissolved salts (TDS) due to a large amount of nickel which invariably accompanies the analytes into the solution in addition to the salt used for fusion. These dissolved salts have to be separated out from the solution employing additional steps like ammonium hydroxide precipitation and group separation of REEs as fluoride prior to determination by ICP-OES and ICP-MS, making the procedures lengthy. Sodium fluoride salt

is an effective flux but requires very high temperatures for fusion. However, sodium fluoride (NaF) when mixed with potassium bi-fluoride (KHF<sub>2</sub>) results in a mixture which melts at much lower temperatures, there-by making it easier to carry out the fusions<sup>15</sup>. Hence, a fusion mixture of KHF<sub>2</sub> and NaF in 3:1 weight ratio has been employed. In the present study, it was found that fluoride mixture fusion resulted in complete decomposition of bauxite samples. The total dissolved salt (TDS) level in the final solution is <0.2% due to the dilution involved and did not pose problems during ICP-MS determinations. It was also observed that the sample solutions prepared by the proposed method showed good stability over a substantial period of time. Procedural blanks were analysed concurrently along with the samples and all determinations were blank deducted. High purity salts were used and extremely low procedural blanks were achievable. Therefore, the determination limits did not suffer much when compared to open acid digestion methods. Further, it was also feasible to use the same solution for determination of major and minor components by ICP-OES.

### Determination of major and minor constituents in Bauxite

For assessing possible interferences that could originate from the matrix, the concentrations of key major and minor constituents in the samples analysed were first determined<sup>16</sup>. The sample solutions were prepared by two methods: one employing the fluoride fusion method and another by an alternate sodium peroxide fusion method<sup>13,16</sup> and the concentrations of key major and minor constituents were determined using ICP-OES. The values obtained are given in Table-2. Samples analysed contained high amounts of aluminum (26.8% to 65.4% Al<sub>2</sub>O<sub>3</sub>) and iron (0.99% to 68.4% Fe<sub>2</sub>O<sub>3</sub>). Bauxite certified reference material “BCS-CRM No. 395” (supplied by Bureau of Analysed Samples Ltd., U.K) was also analysed and values obtained are given in Table-3.

**Table-2 Concentration of Major-Minor Constituents in Bauxite samples (N=3)**

Sample No.	AMD-BX-1		AMD-BX-2		AMD-BX-3		AMD-BX-4		AMD-BX-5	
	Value obtained <sup>a</sup> g g <sup>-1</sup> %	Value obtained <sup>b</sup> g g <sup>-1</sup> %	Value obtained <sup>a</sup> g g <sup>-1</sup> %	Value obtained <sup>b</sup> g g <sup>-1</sup> %	Value obtained <sup>a</sup> g g <sup>-1</sup> %	Value obtained <sup>b</sup> g g <sup>-1</sup> %	Value obtained <sup>a</sup> g g <sup>-1</sup> %	Value obtained <sup>b</sup> g g <sup>-1</sup> %	Value obtained <sup>a</sup> g g <sup>-1</sup> %	Value obtained <sup>b</sup> g g <sup>-1</sup> %
TiO <sub>2</sub>	2.13	2.72±0.11	0.54	0.62±0.05	0.52	0.57±0.05	0.57	0.64±0.05	0.58	0.65±0.07
Al <sub>2</sub> O <sub>3</sub>	33.2	33.7±1.01	45.5	45.7±1.8	65.0	65.3±1.9	62.2	63.1±1.8	26.4	26.8±0.80
Fe <sub>2</sub> O <sub>3</sub>	6.84	6.83±0.21	0.93	0.99±0.09	0.80	0.85±0.07	3.15	2.99±0.3	2.41	2.49±0.30
MnO	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
MgO	0.23	0.29±0.01	0.11	0.12±0.01	0.02	0.03±0.005	0.04	0.05±0.01	0.02	0.03±0.005
CaO	0.07	0.07±0.01	0.06	0.07±0.01	0.04	0.05±0.005	0.05	0.06±0.01	0.03	0.04±0.008
P <sub>2</sub> O <sub>5</sub>	0.26	0.25±0.02	0.12	0.15±0.02	0.08	0.08±0.01	0.05	0.05±0.01	0.05	0.06±0.005

<sup>a</sup> by ICP-OES method employing Na<sub>2</sub>O<sub>2</sub> fusion

<sup>b</sup> by ICP-OES method employing NaF-KHF<sub>2</sub> fusion

**Table-3 Concentration of Major-Minor Constituents in BCS-CRM No.395 (N=3)**

Element	Value obtained <sup>a</sup> g g <sup>-1</sup> %	Value obtained <sup>b</sup> g g <sup>-1</sup> %	Certified value g g <sup>-1</sup> %
TiO <sub>2</sub>	1.91	2.03±0.10	1.93
Al <sub>2</sub> O <sub>3</sub>	51.6	52.1±1.56	52.4
Fe <sub>2</sub> O <sub>3</sub>	16.3	16.4±0.5	16.3
MnO	<0.02	<0.02	<0.02 <sup>R</sup>
MgO	0.02	0.03± 0.005	0.02
CaO	0.05	0.07±0.01	0.05
P <sub>2</sub> O <sub>5</sub>	0.14	0.14±0.02	0.13-0.16 <sup>R</sup>

<sup>a</sup> by ICP-OES method employing Na<sub>2</sub>O<sub>2</sub> fusion<sup>b</sup> by ICP-OES method employing NaF-KHF<sub>2</sub> fusion<sup>R</sup> - Reference values

### Determination of Rare Earth Elements and Yttrium in Bauxite

The solutions of five samples were prepared using the fluoride fusion method. REE and Y were determined directly after appropriate dilution by ICP-MS. For validation, the samples were also analysed by an alternate sodium peroxide fusion method employing ICP-OES. The results obtained for REE and Y contents of five bauxite samples are given in Table-4. The results obtained by present ICP-MS method compared well with those obtained by the alternate ICP-OES method, there-by proving the accuracy of the present method. The high aluminum-iron matrix does not pose problems in ICP-MS unlike in ICP-OES determinations wherein severe spectral interferences are encountered. Hence, for ICP-OES determinations, additional steps to separate and pre-concentrate REE have to be employed making ICP-OES determinations more laborious. In spite of employing additional pre-concentration/separation steps (ammonia hydroxide group precipitation followed by fluoride separation), some REEs like Tb, Tm and Lu could still not be quantified by the ICP-OES method (Table-4). On the contrary, it is feasible to achieve faster direct determination of all REEs by ICP-MS. Further, owing to the superior sensitivity much lower concentrations of REEs can be determined in bauxites by ICP-MS (Table-5).

### Determination of Rare Earth Elements and Yttrium in Bauxite CRM

The analytical method used in the present work was validated by application to a bauxite certified reference material "BCS-CRM No.395". Results obtained for REEs and Y in the CRM by the present method are given in table-6. Though international bauxite reference materials are available, certified or even proposed values are not available for their REE concentrations. Since certified values for REEs are not available for CRM NO.395, it was also analysed by an alternate ICP-OES method and results compared with those obtained by the present method. The values obtained by both methods were in good agreement with each other for all elements except Tb, Tm and Lu. Very low values as in the case of Tb, Tm and Lu could not be quantified by the ICP-OES method as they were below its determination limits. Hence, the CRM was spiked with known amounts of REE and Y and analysed by the present method.

The results obtained are given in Table-5. The recoveries obtained for all elements were within the acceptable range (90-110%), there-by further ascertaining the accuracy of the method. The values reported for REEs and yttrium for BCS-CRM No.395 in the present work can serve as usable values for the above reference material.

**Table-4 Determination of REEs, Y In Bauxite Samples (N=3)**

Sample no.	AMD-BX-1		AMD-BX-2		AMD-BX-3		AMD-BX-4		AMD-BX-5	
	Value found <sup>a</sup> ( $\mu\text{g} \cdot \text{g}^{-1}$ )	Value found <sup>b</sup> ( $\mu\text{g} \cdot \text{g}^{-1}$ )	Value found <sup>a</sup> ( $\mu\text{g} \cdot \text{g}^{-1}$ )	Value found <sup>b</sup> ( $\mu\text{g} \cdot \text{g}^{-1}$ )	Value found <sup>a</sup> ( $\mu\text{g} \cdot \text{g}^{-1}$ )	Value found <sup>b</sup> ( $\mu\text{g} \cdot \text{g}^{-1}$ )	Value found <sup>a</sup> ( $\mu\text{g} \cdot \text{g}^{-1}$ )	Value found <sup>b</sup> ( $\mu\text{g} \cdot \text{g}^{-1}$ )	Value found <sup>a</sup> ( $\mu\text{g} \cdot \text{g}^{-1}$ )	Value found <sup>b</sup> ( $\mu\text{g} \cdot \text{g}^{-1}$ )
La-139	215±11	211	378±19	375	191±9	196	171±8	167	167±8	160
Ce-140	414±20	418	719±36	715	316±16	311	297±15	308	355±18	334
Pr-141	46±5	46	68±3	60	27±1.5	26	28±2	27	35±3	34
Nd-146	199±10	191	209±10	190	82±4	92	94±5	90	128±10	136
Sm-147	41±2	52	29±1.5	33	12±0.6	14	13±0.8	14	22±2	18
Eu-151	10±0.8	12	3.5±0.3	3.0	2±0.2	1.9	2±0.2	1.2	2±0.15	2.8
Gd-157	46±5	48	33±3	34	5±0.5	5	13±1	14	15±1	18
Tb-159	6.7±0.7	8	5±0.5	4	0.7±	<1	3±0.3	3	2±0.2	2.6
Dy-163	34±3	32	30±3	30	3±0.3	2	10±0.8	12	12±1	10
Ho-165	5.1±0.5	5.2	5.6±0.6	6	0.6±0.08	<1	2±0.2	2	2.1±0.2	2
Er-166	11.8±1	13.2	15.1±1.3	16.2	1.2±0.12	1.3	4±0.5	5	7.8±0.8	6.3
Tm-169	1.6±0.1	1.5	3±0.3	2	0.2±0.03	<1	0.6±0.08	<1	0.9±0.1	<1
Yb-172	13.5±1	10	18.7±1.5	17	1.5±0.12	1.6	4.1±0.4	4	7.3±0.7	6.8
Lu-175	1.7±0.4	1.8	3±0.3	2.4	0.2±0.02	<1	0.7±0.1	<1	1.5±0.15	1.3
Y-89	128±7	127	213±11	197	14±1	15	58±3	59	81±4	74

<sup>a</sup> by present ICP-MS method after KHF<sub>2</sub>-NaF fusion

<sup>b</sup> by ICP-OES method after Na<sub>2</sub>O<sub>2</sub> fusion, ammonia group precipitation & fluoride separation

**Table-5 Determination Limits of REEs & Y In Bauxite By the present ICP-MS Method**

Element	On-line Detection limits in ppt	Determination limits in ppm
La	2	0.2
Ce	5	0.5
Pr	0.8	0.08
Nd	7	0.7
Sm	3	0.3
Eu	3	0.3
Gd	1	0.1
Tb	0.5	0.05
Dy	0.9	0.09
Ho	0.1	0.01
Er	0.5	0.05
Tm	0.2	0.02
Yb	0.8	0.08
Lu	0.2	0.02
Y	3	0.3

**Table-6 Determination of REEs, Y In BCS-CRM No.395 (N=3)**

Analyte -Mass No.	Value obtained <sup>a</sup> ( $\mu\text{g g}^{-1}$ )	Value obtained <sup>b</sup> ( $\mu\text{g g}^{-1}$ )
La-139	60±3	57
Ce-140	110±6	103
Pr-141	10±0.5	10
Nd-146	35±2	34
Sm-147	5±0.5	5
Eu-151	1±0.1	1
Gd-157	4±0.5	4
Tb-159	0.8±0.08	<1
Dy-163	5±0.5	6
Ho-165	1.0±0.1	2
Er-166	4.2±0.4	7
Tm-169	0.5±0.05	<1
Yb-172	3.1±0.3	3
Lu-175	0.5±0.05	<1
Y-89	31±1.5	28

<sup>a</sup> by present ICP-MS method employing KHF<sub>2</sub>- NaF fusion<sup>b</sup> by ICP-OES method employing Na<sub>2</sub>O<sub>2</sub> fusion and fluoride group separation**Table-7 Analytical Results By Present Method For BCS-CRM NO.395 Spiked With Known Amounts of REE & Y (N=3)**

Analyte- Mass No.	Values obtained for CRM No.395 ( $\mu\text{g g}^{-1}$ )	Amount Spiked ( $\mu\text{g g}^{-1}$ )	Values obtained for spiked CRM No.395 ( $\mu\text{g g}^{-1}$ )	% Recovery
La-139	60	10	66	94
Ce-140	110	20	127	98
Pr-141	10	5	15.5	103
Nd-146	35	5	41	103
Sm-147	5	2	7.5	107
Eu-151	1	1	2.1	105
Gd-157	4	2	6.5	108
Tb-159	0.8	1	1.9	108
Dy-163	5	1	6.5	108
Ho-165	1.0	1	2.1	105
Er-166	4.2	1	5.6	107
Tm-169	0.5	1	1.6	107
Yb-172	3.1	1	4.4	108
Lu-175	0.5	1	1.6	107
Y-89	31	5	38	105

## CONCLUSION

A fluoride fusion method was applied for the accurate and precise determination of REE and yttrium in iron-aluminum rich matrices such as bauxites by ICP-MS. The method is effective in achieving complete dissolution of bauxite samples. The methodology involved is



simple and rapid as no additional analytical steps have been employed for the separation of the aluminium-iron matrix and pre-concentration of REEs. Further, owing to the superior sensitivity of ICP-MS much lower concentrations of REEs and yttrium can be determined directly in bauxite samples by the present method. In addition, the sample solutions showed good stability and can also be used to simultaneously determine major and minor constituents by ICP-OES.

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#### REFERENCES

1. Henderson, P., Rare Earth Elements Geochemistry, Elsevier, Amsterdam (1984).
2. Voncken, J.H.L, The Rare Earth Elements - An Introduction, Springer briefs in Earth sciences, Switzerland (2016).
3. Deady, E., Mouchos, E., Goodenough, K., Wall, F. & Williamson, B., Developing alternative resources of rare earth elements in Europe –EURARE and the red mud challenge, *Geophysical Research Abstracts*, EGU2015-10235 (2015).
4. Deady, E., Mouchos, E., Goodenough, K., Williamson, B. & Wall, F., Rare earth elements in karst-bauxites: a novel untapped european resource, ERES2014: 1st European Rare Earth Resources Conference, Milos, Greece (2014).
5. Borra, C.R., Blanpain, B. & Pontikes, Y., Recovery of Rare Earths and Other Valuable Metals from Bauxite Residue (Red Mud): A Review, *J. Sustain. Metall.* 2:365-386 (2016).
6. Zhi-jun, G., Jing, C., Hao-feng, C. & Jie, LI, Simultaneous determination of major and minor components in silicate and bauxite by X-ray fluorescence spectrometry with fusion sample preparation, *Metallurgical Analysis*, 35:73-78 (2015).
7. Vukotic, P. Determination of rare earth elements in bauxites by instrumental neutron analysis, *Journal of Radioanalytical and Nuclear Chemistry*, 78: 110-115 (1983).
8. Thompson, M. & Walsh, J.N *A Handbook of Inductively Coupled Plasma Spectrometry (ed. Blackie)*, Glasgow, London, U.K. (1983).
9. Barnes, R.M & Mahanti, H.S, Determination of Rare Earth Elements in Aluminum by Inductively Coupled Plasma-atomic Emission Spectroscopy, *Applied Spectroscopy* 37 : 261-262 (1983).
10. Barnes, R.M & Mahanti, H.S, Analysis of bauxite by inductively coupled plasma-atomic emission spectroscopy, *Spectrochim Acta*: 38:193-197 (1983).
11. Das, D.K & Roychowdhury, P., Determination of Rare Earth Elements in Bauxite by Inductively Coupled Plasma Atomic Emission Spectrometry, *Atomic Spectroscopy*, 18:80-83 (1997).
12. Ochsenkühn-Petropulu, M., Tyberopulu, T. & Parissakis, G., Direct determination of lanthanides, yttrium and scandium in bauxites and red mud from alumina production. *Anal Chim Acta*, 296: 305-313(1994).

13. Mukhedkar, A.J. & Kulkarni, S.B., Use of peroxide flux in the ore analysis beryl, bauxite and ilmenite, *Fresenius' Journal of Analytical Chemistry*, 207:421 (1965).
14. Rao Borra, C., Pontikes, Y., Binnemans, K. & Van Gerven, T., Leaching of rare earths from bauxite residue (red mud), *Minerals Engineering*, 76:20-27 (2015).
15. Srivatsava, P.K., Singh, A.K., & Beena, S., ICP-OES determination of Nb, Ta, Ti, Sn, Zr and Hf in columbite-tantalite and tin slag samples, *Atomic Spectroscopy*, 24(3):98-104(2003).
16. Padmasubashini, V., Beena, S. & G. Chakrapani, G., Chemical Characterization of Bauxite samples using ICP-OES, Proceedings of "International Symposium on Emerging trends in Analytical Chemistry", Bengaluru, India (2016).