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Simultanious multielemental analysis of alumina process samples using inductively coupled plasma spectrometry (ICP-AES)

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ABSTRACT

A number of spectrometric techniques are in use, including flame photometry, furnace atomic absorption and inductively coupled plasma spectrometry. Selecting the most appropriate tool for the analysis of different raw materials, intermediate products and finished products in alumina refinery in India at trace level has become a difficult task for the laboratory chemists, especially since there is considerable overlap of capabilities. The elements such as Fe, Si, Ti, Pb, Mn, V, P, Ga Ca, Cd, Cu, Cr, Ni, Mg etc are detrimental to process for the production of alumina in refinery all over the world. Minor elements are present at very low level (<0.1%). The minor elements are not being able to determine by conventional wet chemical methods with high precision. The major constituents such as Al_2O_3, SiO_2 Fe_2O_3 and TiO_2 are present at very high concentration (upto 40 %) in Bayer's process samples. In this paper, optimization of operating condition of analysis and sample preparation methodology, their significance has been studied. A comparative study of conventional (Wet Chemical-classical) and instrumental (ICP-modern) methods in the determination of major and trace elements for Indian bauxite, hydrate, red mud, Bayer's liquor and product alumina have been discussed.   © 2011 Trade Science Inc. - INDIA

KEYWORDS

INTRODUCTION

Analytical chemistry is the science of accurate, precise, qualitative and quantitative measurements involving chemical systems[1]. Spectroscopy is defined as the interaction of light & matter which has both physical and analytical applications. Physical spectroscopists use emitted light, absorbed light, or scattered light in order to understand the mechanics of a chemical system. Analytical spectroscopists use the same physical processes to determine the content and concentration of the atomic and molecular species present in a chemical system[2]. Inductively coupled plasma spectroscopy (ICP-AES) is an emission spectrophotometric technique; the excited electrons emit energy at a particular wavelength as they return to ground state. The fundamental characteristic of this process is that each element emits energy at specific wavelengths typical to its chemical properties. Although each element emits energy at multiple wavelengths in ICP-AES technique but selecting a single wavelength is most common for a given element. The intensity of the energy emitted at

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the selected wavelength is proportional to the amount (concentration) of that element in the analyte solution. By determining the wavelength which is emitted by a sample analyte and by measuring their intensities, it can quantify the elemental composition of the given sample relative to a certified reference standard. In ICP analysis, the sample is subjected to temperatures as high as 8000-10,000°C, where even the most refractory elements are atomized with high efficiency. As a result, detection limits for these elements can be orders of magnitude lower than other techniques, typically at the 1-10 parts-per-billion level[3]. Digestion methods for advanced ceramic materials and subsequent determination of silicon and boron by inductively coupled plasma atomic emission spectrometry have been studied[4].

In this technique, analysis requires a sample to be in solution. Ore/mineral samples, red mud, hydrate and product alumina must be dissolved in mineral acids. This can be achieved either by acid digestion using HF, H_2SO_4, HNO_3, & HCl acids, or by a $LiBO_2$ or boric acid flux-fusion method. Being hydrofluoric acid somewhat dangerous for routine analysis the acid digestion is not able to produce consistent and reliable data for silica based mineral characterization because it volatilizes in the presence of HF. The fusion technique is applied in dissolution of several raw materials for many reasons instead of using acid digestion.

In alumina refineries, aluminum is being extracted from bauxite using Bayer process and mud generated is more than 70 million tons all over the world[5]. Typically, iron oxide and titanium oxides, silica, calcium carbonate, unrecoverable alumina, caustic soda and other minor elements are present in the residue. The method of analyses of solid samples was microwave digested in an aquaregia solution to leach extractable metals as prescribed in EPA Method 3051[6]. Recovery of lanthanides and yttrium from red mud by selective leaching and characterization of bauxite have been done[7, 8]. In the present communication, a methodology of sample preparation, optimization of procedure and determination for various alumina process raw materials, by-products and products have been studied and discussed.

MATERIALS AND METHODS

Equipments

Elemental determination was conducted on inductively coupled plasma spectrometer (ICP-AES Model Iris-Intrepid-II XDL), Thermo Electron Corporation, USA. The double distilled water was used during all the dilutions purpose was prepared by quartz distillation unit.

Reagents and chemicals

Elemental standards, 1000 ppm (Al. Fe, Si, Ti, Ca, Cd, Cu Cr, Ni, Mg Pb Mn, V, P, Ga) were of high purity (99.99 %). These standards were procured from Thermo Electron Corporation, UK and Qualigens India Ltd. Working standards were prepared by dilution used for calibration, method development and optimization of methods. All the chemical, reagents and standards were of analytical and spectral grade. Bauxite (Central & East Coast -India) Hydrate & Alumina and Bayer's liquor samples were collected from industry. The liquor samples were filtered with micro filter paper. All the dilutions were done using de-ionized water.

METHODS OF SAMPLE PREPARATION

Bauxite & red mud

Major and trace elements characterization in bauxite & Red mud have been carried out using both triple acid digestion and fusion techniques.

Acid digestion

Weighed 0.5 gm bauxite or red mud samples transferred into a 250 ml beaker. Moisten with distilled water, added 15 ml HCl and 5 ml HNO_3 (conc.) and digested gently over hot plate for 20-30 minutes. Added 40 ml H_2SO_4 (1:1), covered and baked to white fumes and continued fuming for 30-45 minutes. After complete fuming beaker was removed from hot plate and cooled. Initially added 5–10 ml cold distilled water, then diluted to 150–160 ml. The whole solution was digested on a low temperature hot plate until the solution become clear. Make up and aliquot and use for elemental analyses.

Fusion method

Weighed accurately 0.2 gm of powdered samples

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of bauxite or red mud and 1.00 gm of anhydrous lithium metaborate into a clean dry platinum crucible and mixed carefully with spatula. Fused the mixture in furnace for 45 minutes min at 1000 ± 10 °C, swirled the whole melts just after taking out from the furnace. Added 100 ml of 5 % w/v nitric acid into a 250 ml beaker put a stirrer rod into the beaker. Completely dissolved solution was transferred to 250 ml volumetric flask.

Bayer's liquor

Pipette out 25 ml sample liquor and filtered into 250 ml volumetric flask, shake well & make up to the mark. Taken 5 ml of diluted sample into a 100 ml beaker and warmed gently for few min, added 5 ml conc. nitric acid and transferred the whole solution into 50 ml volumetric flask. Cooled the mixture and make up to the mark and use for analysis, similarly reagent blank was also prepared with acid and distilled water.

Hydrate & product alumina

Weighed accurately 0.1 gm dried sample within a range of 0.0995–0.1005 g into a 100 ml platinum crucible. Further added 1 gm fusion mixture (Lithium tetra borate + Lithium Meta borate, 1:1) to the crucible. Put the crucible at $500 \pm$ °C in the furnace for 20-25 minutes and at 1000 ± 10°C for another 25-30 minutes. Removed and cooled the crucible, added 50 - 60 ml distilled water and digested on hot plate for 15 minutes. Content was transferred the into 250 ml beaker containing 5 % v/v nitric acid. Repeat the process for 3-4 times to assure that all contents are transferred to the beaker. Aliquot was prepared in 100 ml volumetric flask.

RESULTS & DISCUSSION

The standard operating condition of the equipments was achieved by carrying out number of trial experiments and a optimized condition was obtained. Comparative studies were done for different sample preparation procedure and analysis for bauxite using ICP-AES. Analyses data for major elements furnished for six bauxite samples using ICP is reported in the TABLE 1. Data presented in the TABLE reveals that techniques could be an alternative for determination of various constituents present in the bauxite sample. It is believed that acid digestion take more time and also the risk of

handling over fusion technique. The data were furnished on the sample received for the Indian bauxite for characterization in the laboratory.

Optimized instrumental operating conditions (ICP-AES)

1	Power	1.20	kW
2	Plasma gas flow	15.0	L/min
3	Auxiliary gas flow	0.75	L/min
4	Nebulizer Concentric	Glass-High	Flow
5	Nebulizer gas flow	0.70	L/min
6	Pump speed	20	rpm
7	Sample Delay	30	sec
8	Rinse time	30	sec
9	Sample Replicate time	20	sec
10	Stabilization Time	10	sec
11	Replicates	3	Nos

TABLE 1 : Data for major element determined by ICP using fusion method

Chemical Constituents	Bauxite - 7	Bauxite - 8	Bauxite - 9	Bauxite -16	Bauxite -17	Bauxite -18
	%	%	%	%	%	%
Al_2O_3	42..24	41.96	44.42	39.88	47.25	47.82
Fe_2O_3	31.32	28.46	25.38	25.03	16.45	16.02
SiO_2	1.32	3.15	3.62	9.69	5.12	4.64
TiO_2	2.88	3.26	2.67	6.05	7.43	7.35

Two bauxite samples for major and minor elements were analyzed using fusion method in ICP and data obtained are reported in TABLE 2. In the present study, it was observed that bauxite with low silica could also be analyzed using acid digestion where as high silica bauxite or other ores & minerals could be utilized for fusion method. It is evident from comparative data obtained from acid digestion and fusion are very close and difference in the value varies between 0.02- 0.33. Comparative study was also carried out for bauxite and red mud using conventional (wet chemical) and Instrumental (ICP) methods. The value obtained for different constituents are presented in the TABLE 3. The obtained data indicate that the closeness of the analytical technique in both sample. The difference in value obtained for Al_2O_3, Fe_2O_3 and SiO_2 is between 0.16 to 0.8 % and in case of TiO_2 the difference is even less than 0.3 %, which are very much within acceptable analytical limit.

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TABLE 2 : Comparative data obtained for Bauxites using acid digestion and fusion

Chemical Constituents	Bauxite-64			Bauxite-65		
	Fusion	Acid Digestion	Variation	Fusion	Acid Digestion	Variation
Al_2O_3	42.80	43.10	0.30	45.20	44.95	0.25
CaO	0.15	0.18	0.03	0.35	0.29	0.06
Fe_2O_3	21.90	22.15	0.25	22.65	22.73	-0.08
MgO	0.15	0.12	-0.03	0.12	0.06	0.06
Na_2O	0.34	0.27	-0.07	0.47	0.39	0.08
P_2O_5	1.09	1.01	-0.08	1.20	1.13	0.07
SiO_2	8.13	7.80	-0.33	3.55	3.30	-0.25
TiO_2	2.10	1.99	-0.11	1.98	2.14	-0.16
V_2O_5	0.25	0.24	-0.01	0.28	0.26	0.02

TABLE 3 : Comparative data obtained by wet chemical and instrumental (ICP-AES) analysis

Elements	Bauxite JSW -1			Bauxite JSW-2			Red Mud JSW-3			Red Mud JSW-4		
	WCL (%)	ICP (%)	Variation	WCL (%)	ICP (%)	Variation	WCL (%)	ICP (%)	Variation	WCL (%)	ICP (%)	Variation
Al_2O_3	45.90	46.67	0.77	31.20	30.60	0.60	15.05	15.65	0.6	13.90	15.29	1.39
SiO_2	1.95	1.68	0.27	4.56	4.84	0.28	4.95	4.68	0.27	5.98	5.14	0.16
Fe_2O_3	21.80	21.16	0.64	34.24	34.93	0.69	60.35	60.77	0.42	61.30	60.50	0.80
TiO_2	1.90	1.90	0.00	15.30	15.00	0.30	6.25	6.00	0.25	5.10	5.14	0.04

TABLE 4 : Trace impurities in Bayer's liquor

Bayer Liquor	Fe_2O_3	SiO_2	TiO_2	CaO	P_2O_5	V_2O_5
Liq. (gpl)	0.0035	0.85	0.0015	0.022	0.37	1.15

The major portions of the impurity, such as Silica, Iron, Titanium, Phosphorus, Vanadium, calcium, organic carbon are the most important which affect the precipitation process and the product quality. Critical levels of impurities are present in liquor but beyond the limit it affects the whole process and hydrate quality. Determination of these impurities in the Bayer's liquor is a challenge for the analyst in routine process control analysis for better control using conventional methods. The chemistry of Bayer's process is very complex, thus an attempt has been made to determine these impurities at lower level, the data are presented in the TABLE 4. Trace impurities were estimated using inductively coupled plasma technique is found to be very significant and detrimental for alumina process.

These impurities play very important role in production of alumina and its efficiency in alumina refinery. Generally these impurities come from parent raw material i.e. bauxite and additive. Due to complex nature of impurity analysis quantification at such a low level become difficult by available conventional method. Simul-

TABLE 5 : Concentration of minor elements in bauxite, red mud, hydrate & alumina

Major/Minor Elements	Bauxite	Red Mud	Hydrate	Alumina
	%	%	%	%
Fe_2O_3	M	M	0.0152	0.030
SiO_2	M	M	0.010	0.027
TiO_2	M	M	0.0003	0.010
Na_2O	M	M	0.500	0.350
Cr_2O_3	0.082	0.133	ND	0.0011
P_2O_5	0.105	0.246	0.0012	0.0023
V_2O_5	0.079	0.158	0.0015	0.0025
CaO	0.028	0.224	0.022	0.0350
CdO	ND	ND	ND	ND
Cu_2O	0.007	ND	0.0013	0.0034
MnO	0.037	0.089	ND	0.0028
PbO	ND	ND	ND	ND
MgO	0.033	0.280	ND	0.0093
ZnO	0.006	0.010	0.0009	0.0015

taneous multielements quantification was carried out for each Indian bauxite, red mud, hydrate & alumina which is shown in the TABLE 5. Data indicates that impurities obtained are significant and need to be estimated for better for process control & quality product. ICP is found to be a very suitable cost effective, rapid and

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simultaneous method of quantification of impurities in lower concentration. It can also be utilized for higher concentration. Method was found to be very precise and accurate for alumina process samples. The value varies from 0.0003 to 0.28 %, show the limit of determination using ICP, which is very difficult to obtain with conventional method.

CONCLUSION

1. Inductively coupled plasma spectrometer (ICP-AES) used in quantification for a variety of alumina process sample. Standards operating condition have identified and optimized.
2. The technique have been used for the first time in India for process sample characterization. The results clearly indicate that this technique is useful for rapid, cost effective and simultaneous determination of impurity in Bauxite, Red Mud, Bayer's Liquor and alumina.
3. Different sample preparation technique has been used and data show the accuracy using this technique.
4. Comparative analysis also indicates that it could be an alternative for the characterization of process samples in alumina refinery for lower as well as higher concentration for rapid analysis and better process control.
5. Quantification of different constituents in mentioned material have carried out successfully even below 0.01 % and much higher above 40 %.

ACKNOWLEDGMENT

ABBREVIATIONS

gpl –Gram per liter
ND-Not detected
WCL- Wet Chemical
ICP- Inductively Coupled Plasma
M-Major Elements

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