Specifics of Sample Preparation and Mass Spectrometry Analysis of Trace Impurities in Alumina and Aluminium

T.G. Golovanova[1], T.P. Mukina[2], Yu.A. Chernyshova[3], A.P. Nechitaylov[4], A.G. Suss[5]

1. Head of Physical and Chemical Laboratory, 2. Research Associate, 3. Junior Researcher, 4. Consultant, 5. Director of Technology and Engineering Directorate,
"RUSAL ETC" LLC, Sredny pr., 86, Saint Petersburg, 199106, Russia
Corresponding author: Aleksandr.Suss@rusal.com

Abstract

As part of an import substitution program in UC RUSAL, a large scope of work was conducted to produce a greater variety of products, including special aluminium hydrate, special grades of alumina, alloys, etc. Process and product quality control systems require new laboratory test methods, including the content of heavy, rare earth and trace elements. To deliver this, specialists from RUSAL's Engineering and Technology Center (ETC) conduct research and method development using inductively coupled plasma mass spectrometry ICP MS) for trace impurities in hydrates, metallurgical and special grade aluminas, aluminium and alloys, co-products and by-products of alumina production. Based on ICP MS, new procedures are developed to assist analytical departments at UC RUSAL refineries and smelters. Calcined alumina, metals and alloys can be challenging to analyze, partly because before analysis, special dissolution and preparation methods are required. The physical and chemical testing laboratory of the ETC Alumina department studied the sample preparation of mineral raw materials, metals and alumina products for MS analysis. The samples were prepared by fusion with lithium tetraborate, before acid digestion. To prepare samples of alumina, aluminium and intermediate products of alumina production, comparative tests were performed using different sample preparation methods. To eliminate matrix effects, special techniques were also developed. Certification of these methods as internal standards for refineries/smelters and for their inclusion in the GOST National Standards and Specifications reduces the cost of analytical tests and technology/equipment upgrades for refinery and smelter laboratories.

Keywords: Mass spectrometry, Aluminium hydroxide, Alumina, REE, Heavy and trace elements.

1. Introduction

For a number of years, specialists from the physical and chemical laboratory of OJSC "RUSAL VAMI", and later "RUSAL ETC" LLC have been developing methods for dissolution of solid samples for analysis by atomic absorption spectrophometry (AAS), inductively coupled plasma atomic emission spectroscopy (ICPAES) and inductively coupled plasma mass spectrometry (ICP MS).

For ICP MS analysis of raw materials, SGA, aluminium and alumina products, small masses ($\leq$ 0.1 g) are used. For this reason, sample preparation and homogenization become very important due to the strict requirements to maintain sample representivity and uniformity.

For samples analyzed by the MS method, the unit of measurement is ppm, one millionth or 10^{-6} %. To achieve such detection limits and accuracy of the analysis, having a mass spectrometer is not enough. Although the device is a highly sensitive measuring instrument, the quality and reliability of the results heavily depend on the sample preparation. To ensure such results certain requirements need to be met:

- only reagents of high purity can be used for analysis, it is allowable to use domestically produced acids of GR and ACS grades with additional treatment by distillation without boiling;
- reagents and water for analysis need to be prepared immediately prior to the test;
- disposable polypropylene containers shall be used for analysis;
- calibration solutions and internal standards for ICP MS shall be used for the analysis.

As the mass spectrometer determines small and trace amounts of elements in complex often concentrated matrices, to reduce matrix effects samples are significantly diluted. To dilute samples, dosing devices of fixed volume (50, 100 and 200 µl) with an accuracy to 0.1 µl and of variable volume (from 100 µl to 1000 µl and from 1 cm^3 to 5 cm^3) are used.

2. Objectives

Based on the ICP MS method, new procedures are developed to assist analytical departments at UC RUSAL's refineries and smelters.

3. Experimental

Measurements are performed with a Thermo Scientific iCAP Qc inductively coupled plasma mass spectrometer (ICP MS) with standard (quartz) sample introduction system. The iCAP Qc is a robust, multipurpose quadrupole ICP MS. The spectrometer ensures quantitative determination of almost all elements of the periodic table, within a wide range of concentrations and elemental isotope ratios in various samples. A number of advanced developments are implemented in the spectrometer to ensure excellent metrological characteristics.

Prior to MS determination of trace elements, the sample to be analyzed needs to be solublised. For this purpose standard dissolution methods are applied, such as dissolution in method specific acids or acid mixtures in atmospheric systems or fusion of the sample with flux and subsequent leaching of the melt with 5 % hydrochloric acid.

After dissolution of the sample, the solution containing 0.05 - 0.2 % of analyzed sample (depending on the atomic weight of base components) is sprayed into the flow of argon and introduced to the plasma as a fine aerosol. While the aerosol particles pass through the plasma (about 2 ms), the following processes occur: desolvation of the aerosol, evaporation of the solid particles, atomization, excitation and ionization of atoms. The composition of ions in the plasma is proportional to the concentration of analytes in the solution being analysed. From the central part of the plasma the ions pass to the vacuum system of the mass spectrometer where a beam of positive ions are separated from photons and neutral ions. Then ions pass into the quadrupole mass analyzer where they are separated based on mass/charge ratio. Intensities of ions with the same mass/charge ratio are measured by the registration system and obtained mass spectra are saved to the memory of the control computer.

The spectrometer was calibrated with the range of 1 - 10 µg/l for rare elements and 10 - 100 µg/l for common elements. The measurements were performed in two modes: standard (STDR) and using collision cell (KEDR) with helium with selectivity by kinetic energy to eliminate polyatomic overlaps. Detection limits (DL) for the elements were estimated using 3s criterion based on the three measurements of reference samples.

The analysis is performed for the following;

3.1 Bauxites, Nephelines, Mineral Raw Materials, Red Muds, intermediate Products of Alumina Production

To prepare mineral raw material samples, the experience of the Federal State Unitary Enterprise “All-Russian Research Institute of Mineral Resources” (named after N.M. Fedorovski - FGUP VIMS) and the Federal State Budgetary Institution “A.P. Karpinsky Russian Geological Research Institute” (FGBU VSEGEI) was engaged. The samples were prepared by fusion with lithium tetraborate and by acid decomposition.

For acid digestion, the samples are dissolved in PTFE beakers. A sample of 0.1 g is placed in a beaker and mixed with 0.5 cm^3 $HClO_4$, 3 cm^3 HF, 0.5 cm^3 HNO_3. The beakers are covered with PTFE covers and heated for 30 minutes at 130 °C. The solutions are then evaporated of perchloric acid vapours by heating to 180 °C and cooled and evaporated to wet salts. Then 2 cm^3 HCl and 0.2 cm^3 H_3BO_3 are added and the solutions evaporated to 0.7 cm^3 in volume, placed in polypropylene measuring cups and diluted with water to the specified mark.

Acid digestion is used for the dissolution of bauxite samples from different deposits. Samples of Middle Timan deposit (STBR) and complex mineral samples dissolve partially.

All analyzed elements are almost fully extracted by fusion of the analyzed sample with lithium tetraborate with subsequent leaching of the melt with 5 % hydrochloric acid solution. A 0.1 g sample is placed into a platinum crucible with 0.4 g lithium tetraborate and mixed thoroughly. The sample is then fused in a muffle furnace at 1000 °C for 10 minutes. The melt is leached with 5 % hydrochloric acid solution while heating, the solution is then transferred into a 100 cm^3 flask. Two weighed amounts of each sample and one blank (sample with all used reagents but without analyzed material) are measured simultaneously.

Rare earth metals in red mud are measured in standard mode (STDR) with the use of the internal standards (Table 1).

Table 1. Results of REE in red mud measurements from different refineries by ICP MS.

Element	Measurement mode	Australia	Greece
		Element, mass. %	
La	STDR	0.0032	0.012
Ce	STDR	0.0064	0.046
Pr	STDR	0.0065	0.0026
Nd	STDR	0.0051	0.0073
Sm	STDR	0.0015	0.0016
Eu	STDR	0.0038	0.00045
Gd	STDR	0.0011	0.0016
Tb	STDR	0.00015	0.00034
Dy	STDR	0.0010	0.0017
Ho	STDR	0.00013	0.00044
Er	STDR	0.00043	0.0015
Tm	STDR	<0.000001	0.00021
Yb	STDR	0.00040	0.0013
Lu	STDR	<0.000001	0.00024

3.2 Scandium Concentrate and Scandium Oxide

To determine REE in scandium oxide produced from red mud, the following sample dissolution procedure was developed: a 0.1 g sample was placed into 100 cm^3 glass beaker and mixed with 6 cm^3 HCl + 1 cm^3 HNO_3, covered with watch glass, heated till the dissolution of precipitate or absence of brown vapours. If the precipitation does not dissolve, an additional 1 cm^3 HNO_3 is added. The sample is placed into a 100 cm^3 measuring flask or polypropylene measuring cup. Two weighed amounts of each sample and one blank (sample with all used reagents but without analyzed material) are measured simultaneously.

Measurements are performed in standard mode (STDR) with the use of the internal standard (Table 2).

Table 2. Results of REE measurements in scandium oxide.

Oxide element	Measurement mode	Analyzed components, mass. %	
		Lot 6	Lot 7
Y_2O_3	STDR	0.0042	0.0043
Yb_2O_3	STDR	0.0064	0.0060
Nd_2O_3	STDR	0.0010	0.0010
Pr_6O_{11}	STDR	< 0.0001	< 0.0001
Sm_2O_3	STDR	0.0010	0.001
La_2O_3	STDR	< 0.0001	< 0.0001
ZrO_2	STDR	0.17	0.17
CeO_2	STDR	0.011	0.012
SnO_2	STDR	< 0.0005	< 0.0005
CdO	STDR	< 0.0005	< 0.0005
BeO	STDR	< 0.0005	< 0.0005
ThO_2	STDR	0.13	0.13
Lu_2O_3	STDR	0.0017	0.0015
Gd_2O_3	STDR	0.0016	0.0016
Ho_2O_3	STDR	0.0004	0.004
Eu_2O_3	STDR	< 0.0001	< 0.0001
Tb_4O_7	STDR	< 0.0001	< 0.0001
UO_2	STDR	< 0.0001	< 0.0001
HfO_2	STDR	0.0032	0.0034

3.3 Aluminium and Alloys, Cast Iron

To dissolve samples for determination of trace impurities in aluminium, aluminium alloys and cast iron, an SC180 graphite block for 36 cells with 50 cm^3 beakers (HOTBlok) is used. A 0.1 g sample is placed into a 50 ml polypropylene beaker and mixed with 3 cm^3 HCl + 1 cm^3 HNO_3 (Aqua Regia), covered with polypropylene watch glass, heated till the dissolution of precipitate at 100 °C, and held until complete dissolution of the sample. Two weighed amounts of each sample and one blank (sample with all used reagents but without analyzed material) are measured simultaneously.

3.4 Metallurgical Aluminas and Special Grade Aluminas

To determine trace impurities in smelter grade and special grade aluminas, the analyzed sample is fused with lithium tetraborate with subsequent leaching with a 5 % hydrochloric acid solution. To fuse the sample, crucibles made from 100 - 8 PlAu alloy (as per National standard (GOST) 6563) were used. The crucibles are used for alumina analysis only to prevent sample carry over.

Measurements were performed in standard mode (STDR) with the use of the internal standard (Table 3).

Table 3. Results of thallium and scandium measurement in alumina by ICP MS.

Element	Measurement mode	Analyzed components, ppm				
		Ukraine НГЗ	Ireland Aughinish	Jamaica Windalco	Australia QAL	Brazil Alunorte
Sc	STDR	0.50	1.03	0.88	0.98	0.65
TL	STDR	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02

4. Conclusions

1. Inductively coupled plasma mass spectrometry (ICP MS) is a very sensitive method of elemental analysis of samples, and provides for production and quality control of products with strict impurity profile requirements, including special aluminium hydroxide, special grade aluminas, alloys, etc.

2. The quality of results depend on an efficient dissolution method, the quality of reagents, glassware and standard samples. Advanced laboratory equipment including the system for fine purification of acids, deionized water etc. provides for analytical performance at the desired level.

3. The conducted research and method development work enables analysis of trace impurities in metallurgical and special grade aluminas, aluminium and alloys, products and by-products of alumina production, and co-products of alumina refineries including scandium oxide (99.9 % purity grade), metallic gallium (> 99.999 % purity grade), and pure vanadium pentoxide.

4. It has been recommended to equip central refinery and smelter laboratories of UC RUSAL with mass spectrometers.

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5. References

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