

Quantitative Determination of Metals in Waste Aluminium Dross

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Abstract: Characterization of waste Aluminium dross for recovery of metal and other valuable elements are very important for secondary processing industries. Metallic impurity was determined using both classical and ICP-AES. Sample preparation plays key role in accurate quantitative determinations as it is a heterogeneous material. Different sample size (10 to 50 g) were taken for the analysis of metal and other impurities such as Fe, Ti, Ca, Mg, V, P, Cu, Mn, Na, Ni, Zn etc. The percentage of metallic Aluminium was obtained to be 20-21 % and alumina was around 70 %. In the present paper, sample preparation methodology, equipment operating condition optimization, comparative analysis using both classical and ICP-AES has been studied. Precision of measurement in the dross samples were achieved to be less than 5 % RSD.

Keywords: ICP-AES, Aluminium dross, Alumina

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I. Introduction

Atomic spectroscopy is defined as the interaction of light & matter which has both physical and analytical applications. Spectroscopists use emitted light, absorbed light, or scattered light in order to understand the mechanics of a chemical system [1]. Analytical chemist uses the same physical processes to quantify the content and concentration of the chemical species present in a chemical system. The fundamental characteristic of this process is that each element emits energy at specific wavelengths typical to its chemical properties [2]. Although each element emits energy at multiple wavelengths in ICP-AES technique but wavelengths most commonly single wavelength for a given element. The measured energy emitted at the selected wavelength is relative to the concentration of that chemical entities found 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 given certified reference materials.

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.

In this technique, samples require to be in solution form. Ore/mineral samples, waste dross, residual dross or other material must be dissolved in single mineral acid or combination of it. This can be achieved either by acid digestion using H₂SO₄, HNO₃, & HCl acids or by flux-fusion method.

Dross is produced during Aluminium melting processes [3-4]. Typically 1.5-2.5 % of dross are generated per metric ton of molten Aluminium while processing [5]. It has become an area of interest to the Aluminium producers & secondary processors due to large production of Aluminium metal and dross as well [6]. Mainly dross contains metallic Aluminium and Aluminium oxide and some impurities. The recovery of metal from dross is carried out by conventional metallurgical process all over the world. It is generally considered that dross is a process waste and disposed to sub-contractor after recovery of metal from it.

In the present communication, a methodology of sample preparation, determinations of metallic Aluminium using both classical and ICP-AES methods have been used. Optimization of procedure and determination for metal content and other impurities have been done.

II. Materials And Methods

2.1 Equipments

Elemental determination was conducted by 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.

2.2 Reagents and Chemicals

Disodium, potassium tartrate 25% solution having pH between 6.5 – 9.0, Potassium oxalate 25% solution having pH between 7.5–8.0, Barium chloride 10% solution having pH between 6.5–6.8, Mixed Indicator 0.06% solution of Bromothymol blue and Phenol red, Phenolphthalein solution 1% solution, Standard NaOH solution (approximately 0.5 N), Hydrochloric acid (conc.) reagent grade.

Elemental standard, Al, Fe, Ti, Ca, Mg, V, P, Cu, Mn, Na, Ni, Zn (1000 ppm) of high purity (99.9) was procured from Thermo Electron Corporation, UK and Thermo fisher India Ltd. Working standards were prepared by dilution using de-ionized water for calibration, method and optimization of methods. All sample preparation/dilutions were done using double de-ionized water.

III. Methods Of Sample Preparation

3.1 PROCEDURE

Weigh 20 gm of the sample and transfer into 1000 ml beaker Add Conc. hydrochloric slowly and dissolve the Aluminium by heating the beaker on hot plate. Filter the solid with the help Whatmann filter paper no 41 using Buckner funnel and suction pump. Wash the residue with copious amount of hot distilled water. Transfer the filtrate from Buckner flask to 1000 ml standard volumetric flask, cool and make to volume with distilled water and shake well.

IV. Results & Discussion

4.1 QUANTITATIVE ANALYSIS

4.1a Quantification by double titration method

Pipette out 25 ml in 250 volumetric flask and make to volume with distilled water and shake well. Pipette 25 ml from step (v) into 250 ml volumetric flask and add few ml of Conc. HCl Boil it for 5 minutes, cool to room temperature and make to volume and shake well. Pipette out 100 ml aliquot from step in two 500 ml conical flasks. To the first 100 ml aliquot, add four drop of phenolphthalein and 50 ml of di-sodium potassium tartrate solution. Titrate with standard NaOH solution until a faint pink color appears. At this point add 25 ml of Barium chloride solution stir until the precipitate dissolves. The pink color will disappear while adding barium chloride is added. Continue the titration until the again pink color appears. Note the volume in ml of NaOH and read as R_1 . To the second 100 ml aliquot; add 50 ml of Potassium oxalate and 4 to 5 drops of mixed indicator. Titrate with standard NaOH solution. When the yellow color begins to sharpen, slow down addition of standard NaOH as the end point nears. The color change at the end point is from amber to violet. Note the volume in ml from the burette of standard NaOH and read as R_2 .

CALCULATIONS

$$\%Al = \frac{R \times N \text{ of NaOH} \times 0.017 \times 100 \times 1000 \times 250 \times 250 \times 54}{\text{Wt. of Sample} \times 25 \times 25 \times 100 \times 102}$$

Where $R = R_1 - R_2$

4.2 INSTRUMENTAL METHOD

4.2a Quantitative analysis by ICP-AES

Standard operating condition of the ICP-AES was achieved by carrying out number of repeat analysis using single wavelength. Sample in duplicate were prepared and same were used for titration and instrumental analysis for metallic Aluminium. Other impurities are determined by ICP-AES. Analysis data obtained by both the methods are presented in the table-2.

4.2b Optimized operating conditions (ICP-AES)

The optimized parameters of equipment (ICP-AES) achieved for waste Aluminium dross after number of trial experiments are as below.

○ Power	950	W
○ Plasma gas flow	15.0	L/min
○ Auxiliary gas flow	0.65	L/min
○ Nebulizer Concentric	Glass-High Flow	
○ Nebulizer gas flow	0.55	L/min
○ Pump speed	24	rpm
○ Sample Delay	28	sec
○ Rinse time	25	sec
○ Sample Replicate time	15	sec
○ Stabilization Time	3	sec
○ Replicates	3	Nos.

4.2c Analytical Wavelengths Selection

The Wavelength selection is always play big role in intensity of light which is some time an individual choice may varies from one user to other. However, most of the time agreement regarding the wavelength suitable for an exacting element in view of sample matrix and interfering elements. All the wavelength of Aluminium, Al 167.081, 168.215, and 396.152, nm was used for calibration and intensity was recorded to understand the suitability of particular wavelength with respect to inter-elemental interferences. The Counts was obtained to be very high for the spectral line 396.152 nm in such matrix. For other elements, wavelength such as Fe (259.9 nm), Ti (334.9 nm) Ca (393.3 nm) Mg, (279.5 nm) V (292.4 nm), P (177.4 nm), Cu (324.7nm), Mn (257.6 nm), Na (588.9 nm), Ni (231.6 nm) and Zn (213.8 nm) have used. The selected wavelengths resulted good repeatability and reproducibility repeat measurements.

4.2d Standardization & Calibration

In ICP-AES, the instrument response (measured in “counts” units) has been calibrated against known standards. The intensity of lines 396.152 nm of standard solution was determined by the instrument and a simple first order linear regression fit has been utilized to recount the intensity of the elemental concentration. R² value obtained to be the indicative of how data is fit for the linear curve. The calibration plot is presented in the Figure 1. The operating conditions of the ICP during the calibration and measurement of unknown set identical during analysis conditions, so all operation of gas flows, pump speeds could not interfere the final determination. Calibration report of standard samples is given in table-1.

Table-1 Calibration of Aluminium using 10 ppm standard

Element	Line	Unit	Obtained values			Average	SD	% RSD
Al	396.152	Cts/Sec	10.02	9.99	10.01	10.01	0.115	0.104

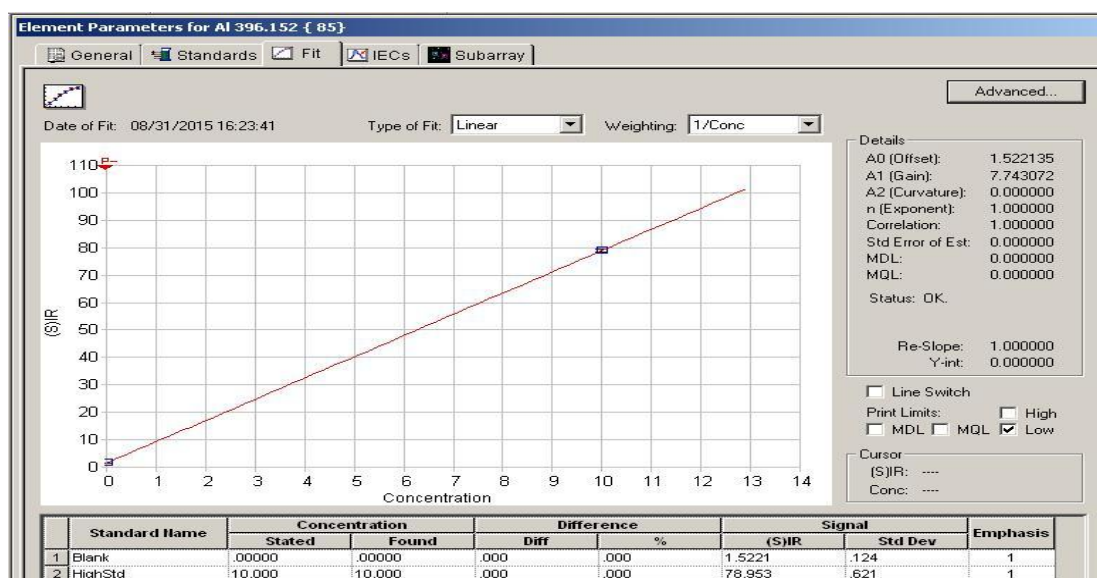


Fig: 1 Calibration plot for Aluminium using single and multiple standard solutions

4.2e Quantitative Analysis:

After calibration starts run as soon as possible, usually it requires 3-5 min. This is of vital importance because the first item in the sample file is a drift solution, which will be used as the master drift to correct the entire run.

Table-2 Comparative analytical data for Aluminium metal by wet chemical & Instrumental methods (ICP-AES)

Sample	Type	Analytical Method	Unit	Nos. of measurement	Measured Value	Std Deviation	% RSD
WASTE ALUMINIUM DROSS	Sample-1 original	Classical	%	2	21.65	ND	ND
		ICP- AES	%	3	21.25	0.025	0.75
	Sample-2 Residual	Classical	%	2	1.05	ND	ND
		ICP -AES	%	3	0.85	0.045	0.89

During analysis, Inter-elemental effect particularly Copper and Molybdenum was also noticed in case of leach liquor of dross but the concentration of these elements found to be very low. Total time taken for single measurement for waste Aluminium dross was less than 30 min. The data obtained from both classical and ICP-AES methods are presented in the table-2. Trace elements simultaneously quantified using ICP are presented in the table-3.

Table-3 Analytical data for trace elements in aluminium dross analyzed by ICP-AES

SN	Trace Elements	(%) Conc.	SD	% RSD
1	Ca	0.74	0.005	0.66
2	Cu	0.02	0.008	0.69
3	Fe	0.19	0.0024	1.21
4	K	0.50	0.056	1.10
5	Mg	0.22	0.0073	1.39
6	Mn	0.004	0.007	1.48
7	Na	0.30	0.0215	1.02
8	Ni	0.13	0.035	2.04
9	Ti	0.012	0.0012	4.05
10	Zn	0.060	0.009	1.04

Since analysis carried out at very high temperature (8000-10000^oK) the inter-elemental effects are observed to be negligible and data obtained for each element are very reproducible.

V. Conclusion:

The Inductively coupled plasma spectrometer (ICP-AES) has been employed for accurate quantification of aluminium dross. Both classical and instrumental have been utilized for the determination of metallic Aluminium. Instrumental method (ICP-AES) was found to be rapid, precise and accurate as compared to wet chemical method. Classical method required more time (2-3 hrs) for sample preparations and titrimetry. Statistical data such as SD < 0.5 & RSD < 5% also indicates the precision of the measurements.

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