



Sodium Analysis in Calcined Alumina using the Spectrolaser

Background

Sodium is an example of a light element that is easily determined by Laser Induced Breakdown Spectroscopy (LIBS) to ppm levels. Largely sodium levels are determined in refractory materials such as alumina by acid digestion techniques or alternatively XRF (x-ray fluorescence). Acid digestion techniques are laborious and thus the total analysis time is quite long. Even sophisticated XRF instruments can take 20 minutes or more to get reliable Na readings owing to relatively weak fluorescence. In contrast, using Spectrolaser instruments multi-element analyses of materials including sodium levels can be obtained in a matter of seconds.

Material

Powdered samples of high-purity Calcined Alumina were received from a Canadian site of a multi-national aluminum producer for analysis with the Spectrolaser. A subset of 8 samples with the same particle size and matrix was chosen for these tests to determine the efficacy of the Spectrolaser in characterizing the sodium content in these materials.

Analysis Method

Each of the samples was pressed, as received, in 40 mm sample cups using the LAT 40T hydraulic press to a pressure of 30 tones and for a dwell time of 30 seconds. Each pellet was analyzed 5 times using 100 laser pulses corresponding to a 20 second analysis time for each measurement.

Detectable Elements

Detectable elements in the materials include the principal components Al, O, Na and Ca. Trace levels of a variety of elements including Fe, Mg, Si and K are also observable.

Calibration and Analysis Tests

Two different calibration methods were used on the sample data, traditional single variant OES (optical emission spectroscopy) analysis utilizing sodium elemental emission, as well as partial least squares chemometric analysis. The results from both methods were reported for comparison.

Using the traditional OES analysis method, the Spectrolaser software was used to select sodium emission lines which were then processed using peak integration, and in this case, normalization to the dominant Al component. The Spectrolaser software automatically constructed calibration curves of the

normalized peak areas vs. concentration of sodium in the alumina standards. The concentration of sodium in the unknown samples was then measured by the instrument using this calibration reference.

Chemometric techniques use statistical methods to look for correlations between element concentrations and spectral features over the entire observed spectrum. The partial least squares method was used in this instance to establish the correlation of the measured spectra from the alumina standards to the given sodium concentration in each standard. The resulting correlation was then used by the instrument software to calculate the level of sodium in unknown samples subsequently analyzed by the instrument.

Calibration Curves

Calibration curves for the two analysis methods are shown in Figure 1 and 2. Both methods yield excellent and reproducible instrument calibration.

Reproducibility

The two calibration methods were used to analyze the data obtained from five measurements of a known alumina standard. The comparison is shown in the table below.

Table 1: Comparison of Na₂O concentration in an alumina standard as measured by the Spectrolaser and analyzed using OES and chemometric calibration techniques.

| | OES (589nm Na line, normalized to 396nm Al line) | Chemometric |
|-----------------|---|-------------|
| 1 | 0.43 | 0.41 |
| 2 | 0.40 | 0.40 |
| 3 | 0.43 | 0.41 |
| 4 | 0.40 | 0.39 |
| 5 | 0.43 | 0.41 |
| Mean | 0.42 | 0.40 |
| SD | 0.02 | 0.01 |
| Reference Value | 0.41 | |

Both methods yield acceptable relative standard deviation levels. In the OES case, three measurements would normally be undertaken and the average reported resulting in a measurement RSD < 3%.

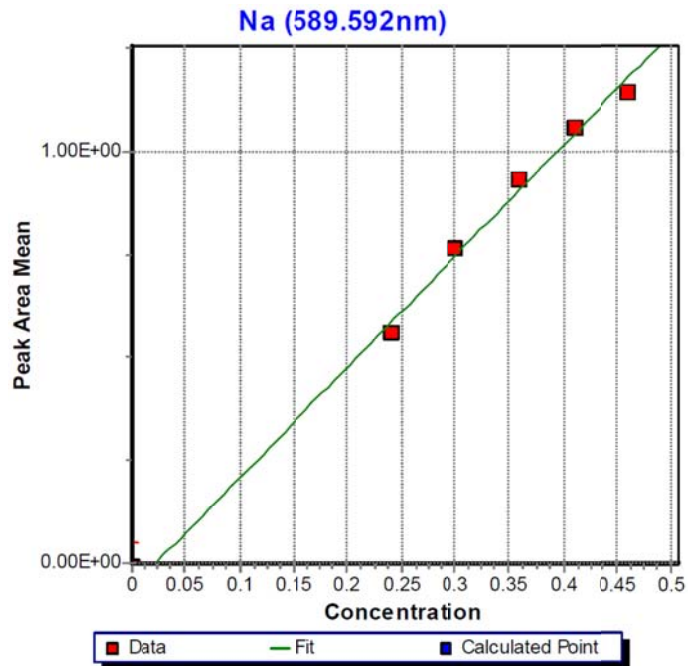


Figure 1. Calibration curve for Na₂O in Calcined Alumina using the 589nm Na emission line.

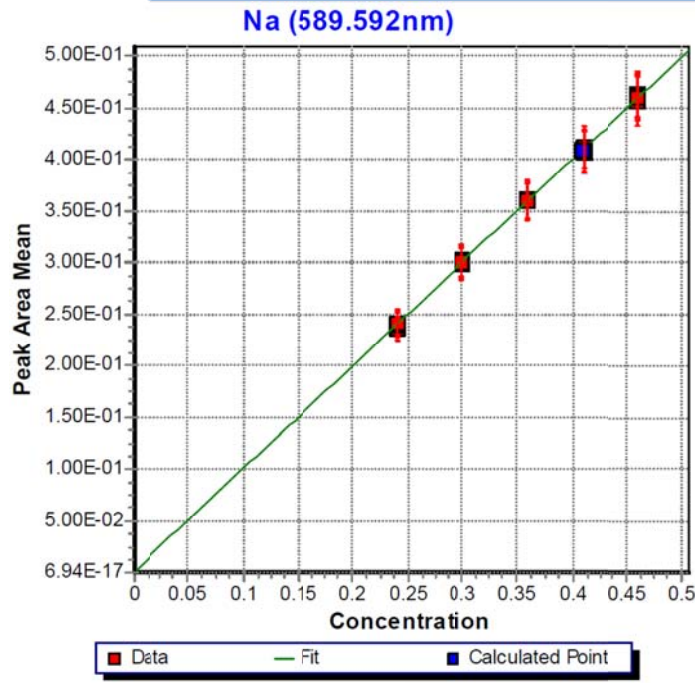


Figure 2: Calibration curve for Na₂O in Calcined Alumina using chemometric techniques