Fluorine Analysis Using Laser Induced Breakdown Spectroscopy (LIBS)

Introduction
Fluorine is found in many mineral and biological samples. Both qualitative and quantitative analysis of fluorine have become essential due to its widespread use in man-made items such as dental care products, pharmaceuticals, and polymers. Fluorine analysis plays an essential role in determining the age of teeth and bones, assessing composition changes in corrosion-affected layers of nuclear reactors, and understanding biochemical effects in living organisms. To date, the most common approaches for fluorine chemical analysis include extensive sample treatment to convert the sample into the appropriate form for analysis (dissolution, separation, pre-concentration, etc.) by ion-selective electrodes, volumetric analysis, ion chromatography, or gas chromatography. Even with all the required sample preparation for analysis, the conventional “go to” atomic spectroscopy methods, such as ICP-OES or ICP-MS, have difficulty ionizing or exciting fluorine due to its high ionization potential (17.42 eV) as compared to Ar (15.76 eV) which is typically used as the plasma gas.
Laser Induced Breakdown Spectroscopy (LIBS) is a great alternative technique to conventional approaches due to many benefits that include rapid speed, multi-elemental detection, direct solid sampling capability, and high analysis throughput. In this technical note, we demonstrate the use of LIBS to efficiently detect fluorine, at 685.6 nm, under a controlled helium atmosphere.

**Operating Parameters**

**Applied Spectra Inc.’s J200 Tandem LA - LIBS Instrument**

- 213 nm Nd:YAG laser (ns)
- Standalone LIBS measurement mode
- 85 µm spot size
- Flex sample chamber with helium gas flow
- Laser sampling grid of 9 locations
- LIBS data analyzed with Applied Spectra Data Analysis Software package

**Calibration Method**

Figure 1 displays the LIBS spectrum collected from analyzing the NIST SRM 120c (phosphate rock) (3.8 wt. % F), with many fluorine emission lines detected. NIST SRM 1835 (borate ore) (0.348 wt. % F) and NIST SRM 2695 (fluoride in vegetation, Low 0.0064 wt. % and High 0.0277 wt. %) were also analyzed for fluorine detection. However, the fluorine in the NIST SRM vegetation “low” sample was not detectable. Therefore, three standards, the phosphate rock, borate ore, and vegetation high, were used for method evaluation and to derive limit of detection (LOD) and quantification (LOQ) in this experiment.

![Applied Spectra Inc.’s J200 Tandem LA - LIBS Instrument](image-url)

**Figure 1.** Example LIBS spectrum (50 laser pulses accumulated) acquired from NIST SRM 120c (Florida Phosphate Rock).
NIST SRM 120c and NIST Vegetation High samples were used to create a set of calibration standards ranging from 0.028 – 3.8 wt. % F mixed with paraffin binder to dilute the samples. Advanced multivariate analysis including a partial least squares (PLS) linear regression routine was performed to generate a calibration curve for fluorine using the entire LIBS spectra from each sample instead of integrating specific emission peak(s) of interest, (Figure 2). Multivariate calibration was performed using the reference samples with known fluorine composition, described above. The multivariate approach can be more accurate, robust, and reliable in comparison to univariate calibration. Multivariate calibration can be performed correctly, even when spectra are only partially resolved, as can be seen for some emission lines in Figure 1.

![Figure 2. Calibration curve (multivariate) developed using Applied Spectra’s Aurora (data analysis) software. Data points represent 50 laser pulses per location, 6 locations per samples over a 1 mm x 1 mm area, and an 85 µm spot size.](image-url)
Figures of Merit

To test accuracy and precision of the multivariate model used for the calibration, two of the prepared standard samples were treated as unknowns. Table 1 displays accuracy and precision results. The multivariate calibration method shows promising results with accuracy < 10 % BIAS and precision < 4 % RSD.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Actual Concentration (ppm)</th>
<th>Measured Concentration (ppm)</th>
<th>% RSD</th>
<th>% BIAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borate Ore</td>
<td>3480</td>
<td>3769 ± 151</td>
<td>4.0</td>
<td>8.3</td>
</tr>
<tr>
<td>S 4</td>
<td>15280</td>
<td>15977 ± 532</td>
<td>3.3</td>
<td>4.6</td>
</tr>
<tr>
<td>S 7</td>
<td>26740</td>
<td>24200 ± 825</td>
<td>3.4</td>
<td>-9.5</td>
</tr>
</tbody>
</table>

The detection limits were determined for fluorine. Since blanks are typically not available for laser ablation techniques, the standard deviation of the background (noise) is used instead of the standard deviation of the blank. The LOD was found to be 135 ppm F and the LOQ was found to be 451 ppm F.

Conclusion

Laser-induced breakdown spectroscopy was demonstrated as a means for detecting and quantifying fluorine. LIBS is a standalone technique, but also can be used as a complementary method to laser ablation ICP-MS. This capability allows the tandem use of these technologies to be harnessed to quantify difficult elements such as fluorine. The LOD determined for this 213 nm LIBS configuration is on par with the LODs published for fluorine detection via LIBS.