LIBS measurements on slag with SilverLIBS (new prototype)

**Experimental optical set up**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Optical Set up** | **(mm)** |  | **Position,  “optimal” parameters** | **(mm)** |
| L1 | -25 |  | Height, z-steg | 85.8 |
| L2 | 50 |  | Height z-steg until sample | 105.4 |
| L3 | 500 |  | Between M1 and sample | 500 |
| M1 | 500 |  | Between L3 and M1 | 102.6 |
| M2 | 117.9 |  | Between L1 and L2 | 30 |
|  |  |  | Between L2 and L3 | 20 |

**Measurements parameters**

|  |  |
| --- | --- |
| **Laser** | SilverLIBS – Litron DPSS |
| *Repetition rate* | 200Hz |
| *Q switch delay* | 295 us |
| *Attenuator* | No |
|  |  |
| **Spectrometer** | IBSEN CMOS - UV (4096 pixels) |
| *Triggering* | External – diode |
| *Time delay* | 1430 us |
| *Exposure time* | 1 ms |
| *Number of spectra* | ca. 1000-1500 |
|  |  |
| ***Sample holder*** | Paper plate |
| ***Translation*** | x-y using motorized stage or manual if very small amount of samples |

**Samples used in these tests**

The samples include in these tests: slag samples from Uddeholm, Paroc, Höganäs, Outokumpu as well as pure materials (iron, magnesium, titanium, nickel, copper, zink, aluminium).

One can find the composition of the slag samples used in these tests as well as their order of measurements in an excel file Litron\_SilverLIBS\_testprover in the following map:

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**Identification and Selection of peaks for analysis**

In the following table, the peaks chosen for the analysis are listed. One can identify more peaks of course, but here are the ones that present less overlap with other elements. For the reference, Ca was chosen. Two lines can be considered as reference: 317.93 nm and 422.61 nm. The 422.61 nm should in theory be a better choice since it has less overlap with other peaks. In the analysis, a threshold could be chosen regarding the intensity of the Ca line (minst 5000 cts for example). The peak intensities were not baseline corrected.

One can find the excel file toppar using in this analysis under

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|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Element | Si | Ca | Al | MgII | MgI | Fe | Cr | Mn |
| Wavelengths | 288.12 | 315.83 | 308.16 | 277.98 | 285.18 | 256.19 | 425.39 | 403.02 |
|  |  | 317.93 | 309.25 | 278.73 |  | 259.81 |  |  |
|  |  | 422.61 |  | 279.48 |  | 262.47 |  |  |
|  |  |  |  | 279.74 |  | 263.05 |  |  |
|  |  |  |  | 280.27 |  | 274.87 |  |  |
|  |  |  |  | 383.75 |  | 309.95 |  |  |
|  |  |  |  |  |  | 312.48 |  |  |
|  |  |  |  |  |  | 372.03 |  |  |
|  |  |  |  |  |  | 373.69 |  |  |
|  |  |  |  |  |  | 374.93 |  |  |
|  |  |  |  |  |  | 404.51 |  |  |
|  |  |  |  |  |  | 426.17 |  |  |

* Silicon

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Figure 1. Calibration curve for the ratio Si 288.12/Ca 317.93. On the left, all spectra (except those saturated for the reference peak) were considered. On the right, only spectra where the Ca peak has a minimum intensity of 5000 cts were considered. Surprisingly, it does get worse when applying a threshold.

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Figure 2. Calibration curve for the ratio Si 288.12/Ca 422.61. On the left, all spectra (except those saturated for the reference peak) were considered. On the right, only spectra where the Ca peak has a minimum intensity of 5000 cts were considered.

When considering the Ca line at 422 nm (atomic line), one can clearly see two “populations of samples” and draw “two calibration curves”. The second population with higher Si content corresponds to the samples from Paroc (P1, P2, P3, P4, F100) for which Si is actually main element and not Ca. The Paroc samples are also the ones that have high content of iron (ca. 10%).

In Figure 3, two calibration curves were considered. The calibration curve in blue corresponds to the slag samples from Höganäs, Outokumpo and Uddeholm, and is quite good (at least as good as in the previous slaggLIBS project).

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One can also investigate the effect of line interference with Fe. In the following figures, the calibration curves were corrected for line interference with Fe.

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Figure 3. Calibration curves for the ratio Si 288.12/Ca 317.93 after correction for Fe line interference. The Fe 262.47/Ca 317.93 ratio was selected for the correction. Two fits are shown.

Note: here I am not sure the quadratic fitting makes sense. The Si 288.12 line does seem to be suffering from self-absorption (see Figure 4: comparison of LIBS for two Uddeholm slag samples with low and high Si/Ca ratio).



Figure 4. LIBS spectra measured for Uddeholm slag samples with low and high Si content. Zoom in the wavelength region 285-290 nm. In blue, the sample U01 has a Si/Ca content ratio of ca~0.9 while in red the sample U03 has a Si/Ca content ratio of 0.2.

* Magnesium

For magnesium, it is difficult to find a correlation between the LIBS ratios and the XRF measurements. Figure 5 shows tentative of “calibrations curves” for the ratios Mg 383.75/Ca 315.83 and Mg 383.75/Ca 422.61.

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Even after line interference correction for Cr using the ratio Cr 425.39/Ca 422.61, the correlation remains very bad. Taking a baseline does not seem to improve the correlation either.

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* Aluminium

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For Aluminium, it is also Paroc samples that have highest content, higher than silicon.

* Mangan

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* Iron

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* Chrome