

MIXED STEEL ANALYSIS USING THE TSI® LIBS DESKTOP ANALYZER

APPLICATION NOTE LIBS-022

Rapid and accurate determination of steel alloy composition and type can be crucial to efficient furnace operation. LIBS offers a fast and robust way of measuring these characteristics without much sample preparation, and with actual measurements in seconds.

Samples

Ten different steel samples varying widely in composition – from low alloy steel and tool steel to high alloy steels rich in Cu, Ni, and Cr were used to build a robust calibration for the TSI® LIBS Desktop Analyzer.

Table 1: Steel Sample Concentrations

	C	Cr	Co	Cu	Mn	Mo	Ni	P	Si
Sample 1	0.41	1	0.008	0.224	0.94	0.229	0.16	0.007	0.242
Sample 2	0.128	2.09	0.01	0.177	0.441	0.89	0.197	0.012	0.255
Sample 3	1.54	11.07	0.07	0.063	0.28	1.09	0.21	0.021	0.29
Sample 4	0.42	0.87	0.012	0.15	0.8	0.25	1.71	0.011	0.24
Sample 5	0.18	0.5	0.012	0.03	0.76	0.13	0.55	0.014	0.25
Sample 6	0.309	13.35	0.02	0.098	0.48	0.034	0.21	0.019	0.72
Sample 7	0.042	15.6	0.04	3.35	0.56	0.11	4.53	0.021	0.42
Sample 8	0.055	24.5	0.19	0.074	1.78	0.2	20.5	0.023	0.47
Sample 9	0.023	17.44	0.31	0.43	1.54	2.08	11.21	0.026	0.46
Sample 10	0.07	17.20	0.16	0.407	1.75	0.54	8.42	0.02	0.59

Table 1 lists selected elemental concentrations from the 10 steel samples.

Sample Preparation

Samples as received presented a clean, flat surface for analysis (i.e., no slag was present on the samples). No additional surface cleaning was done on the samples. Before each analysis, 10 automated laser shots were used to eliminate any surface contamination.



Sample Analysis

The samples were analyzed with a TSI LIBS Desktop Analyzer, model 3966-01, which uses a 50 mJ 266 nm Nd:YAG laser and an echelle spectrometer coupled to an ICCD. Instrument settings were as follows:

- Laser output: 100%
- Spot size: 200 μm
- Sample shots: 50 (shots per spot following cleaning)
- Layout: 8 x 5 grid (40 spots total)
- Spacing: 0.5 mm x 0.5 mm
- Acquisition delay: 1 μs , acquisition gate 10 μs

Data Analysis

Data was analyzed using TSI's chemometric software package into which complete spectra (40 per sample) were exported. Concentration values were entered (as shown in Table 1). The data was analyzed by using half of each of the ten datasets (i.e. a random selection of 20 spectra per sample) for building a calibration using the Partial Least Squares (PLS) model. The resulting calibration curve was then used to predict the sample value of interest by applying it to the second half of each dataset.

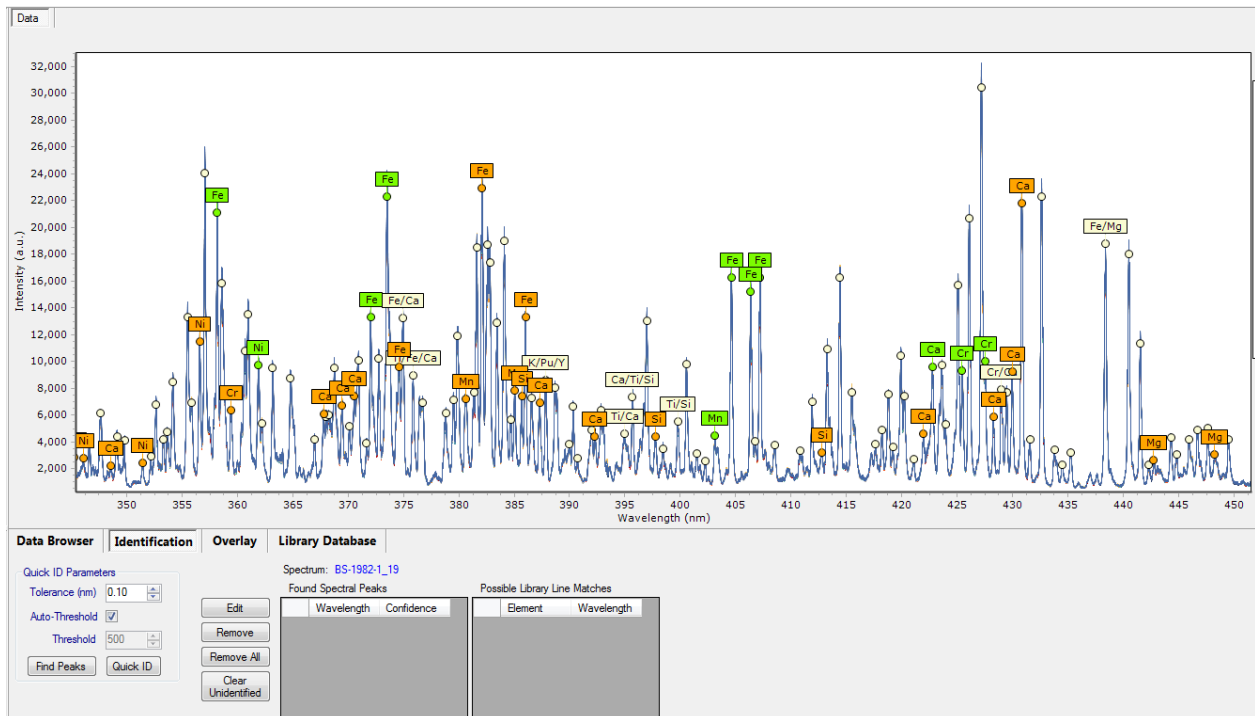


Figure 1: A partial spectrum of one of the steel samples with a few of the peaks identified.

Figure 1 shows a detail of one of the steel spectra. Using the full range of 200 to 900 nm, peaks from all of the elements of interest can be identified. The multivariate calibration model allows for consideration of multiple peaks as well as for differences in the background spectrum for each metal type caused by the changing measurement matrix.

Correlation coefficients for the comparison of predicted versus measured values are shown in Table 1, with very good results for all applications. Other characteristics, such as ash content or sulfur content, will need more samples to give reliable results. Especially sulfur, which could not be measured directly with the spectrometer used, is harder to determine.

Table 1: Correlation coefficients r^2 for predicted values versus measured values.

	C	Cr	Co	Cu	Mn	Mo	Ni	P	Si
r ²	0.9765	0.9973	0.9918	0.9951	0.9948	0.9943	0.9975	0.9802	0.9885

Correlation plots for four of the nine elements of interest are shown in Figure 2 below.

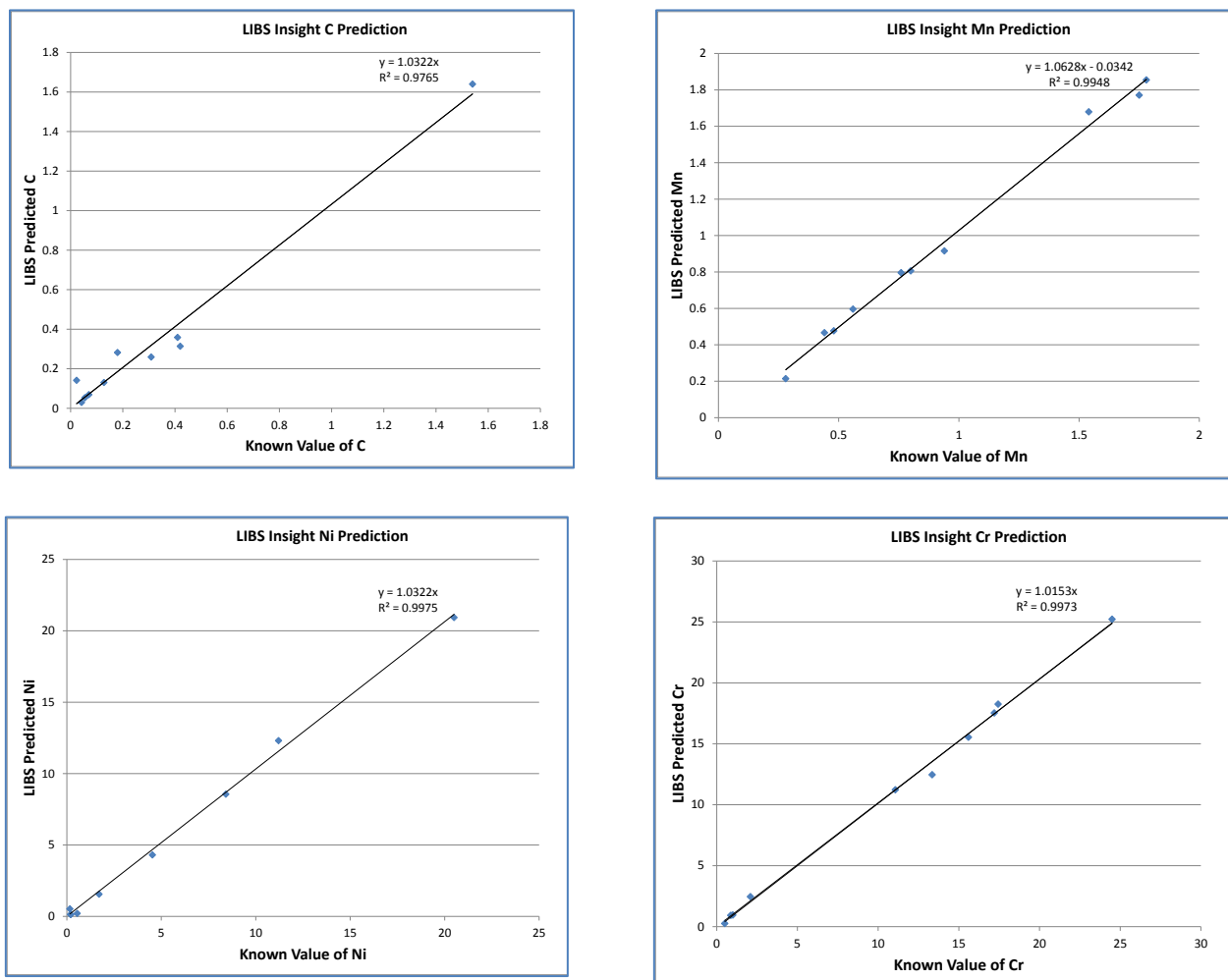


Figure 2: Plots of predicted values (y-axis) versus measured values (x-axis) of elemental concentrations evaluated. Shown are measurement of C, Mn, Ni, and Cr. Of all of the 9 elements quantified, C had the worst R² at 0.9765, while Ni had the best R².

Notably, the predicted versus measured values all lie on 45-degree lines that go through the (0,0) origin, indicating that the predictions are quite good. The standard deviation of the predictions are in the 2 to 3% range for all elements. The quality of the predictions will continue to improve with additional data.

Our chemometrics software also offers other multivariate analysis methods. In addition to calibration curves, classifications of the samples analyzed can be built. Two methods were tested on these samples, the Principal Component Analysis (PCA) and Partial Least Squares Discriminant Analysis (PLS-DA).

PCA nicely separates the ten metal samples from each other (see Figure 3). The three factors depicted account for more than 97% of the variation between the samples.

Table 2 shows the result of the PLS-DA classification. Each of the steel types was assigned a different “class.” The model was built around the calibration data set and tested with the unknown set, as before. The table shows that all sample tests were classified correctly, with the exception of one sample that was labeled “No Match.” In practice, a sample not identified could be interrogated again and identified.

Conclusions

Nine steel samples of a variety of compositions, from low carbon and tool steel to several high-alloy steels of various compositions were analyzed using LIBS. Essentially no sample preparation was required. Using partial least squares (PLS) for quantification, all nine elements tested could be closely predicted, all with $R^2 > 0.97$ and most with $R^2 > 0.99$. Using Principal Component Analysis (PCA) and PLS-Discriminant Analysis (PLS-DA) for qualitative analysis, samples were classified and showed a very good separation and identification. These results were obtained with a very limited data set. Increasing the number of analysis points, and analyzing several samples of similar steel types should improve the results further. LIBS has been shown to be a fast and simple way of determining both the type (classification) of steels, as well as the concentration of major and minor elements in steel.

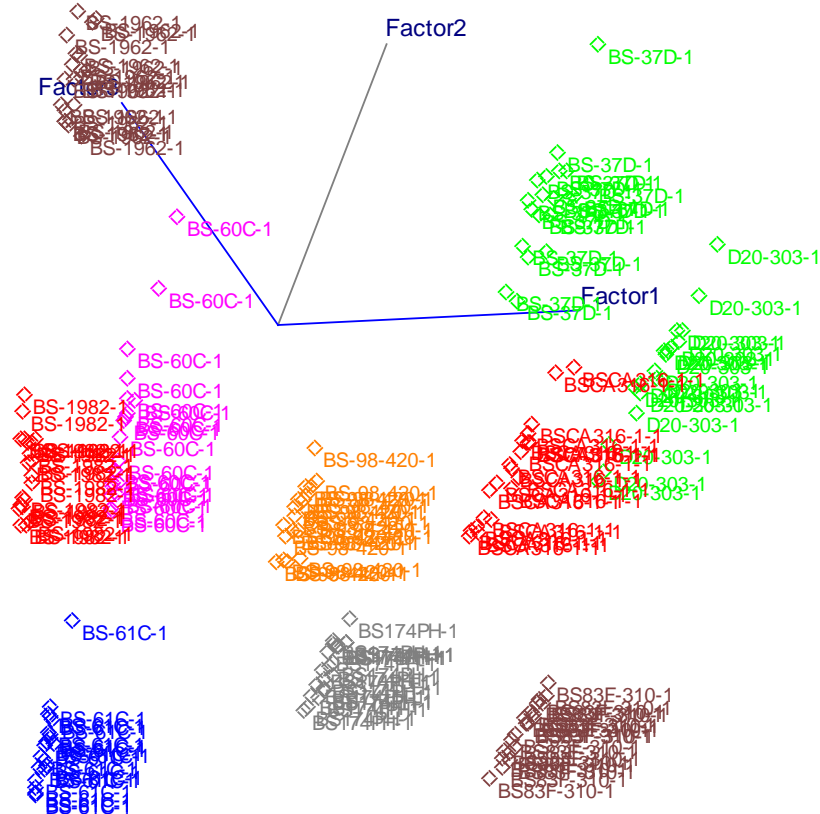


Figure 3: Principal component analysis of the 10 steel samples.

Table 2: PLS-DA classification results for steel samples.

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		1	2	3	4	5	6	7	8	9	10	11	12
		Pred1@9	Pred2@7	Pred3@9	Pred4@7	Pred5@9	Pred6@9	Pred7@9	Pred8@9	Pred9@9	Pred10@9	No match	
1	Actual1	20	0	0	0	0	0	0	0	0	0	0	
2	Actual2	0	20	0	0	0	0	0	0	0	0	0	
3	Actual3	0	0	20	0	0	0	0	0	0	0	0	
4	Actual4	0	0	0	20	0	0	0	0	0	0	0	
5	Actual5	0	0	0	0	20	0	0	0	0	0	0	
6	Actual6	0	0	0	0	0	20	0	0	0	0	0	
7	Actual7	0	0	0	0	0	0	35	0	0	0	0	
8	Actual8	0	0	0	0	0	0	0	20	0	0	0	
9	Actual9	0	0	0	0	0	0	0	0	19	0	1	
10	Actual10	0	0	0	0	0	0	0	0	0	20	0	
11	Unmodelle	0	0	0	0	0	0	0	0	0	0	0	
12													
13													



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