Determination of Elemental Composition of Shale Rocks by Laser Induced Breakdown Spectroscopy (LIBS)

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Abstract

Organic rich shale formations are unique in the production of natural gas because these not only serve as a source for the gas but also form the reservoir. In this study laser induced breakdown spectroscopy (LIBS) was used for elemental characterization of ten outcrop samples from the Marcellus Shale. Powdered samples were pressed to form pellets and used for LIBS analysis. Partial least squares regression (PLS-R) and univariate calibration curves were used for quantification of analytes. The Limit of detections (LOD) obtained for Si, Al, Ti, Mg and Ca were 60.89, 32.97, 15.55, 4.18 and 0.03ppm respectively while for carbon it was 0.52wt%. The samples were also analyzed using ICP-OES and a comparison between LIBS and ICP-OES results is in accordance. Matrix effect was substantially reduced using partial least squares calibration method and predicted results with LIBS gave an accuracy error within 12%. Development of a LIBS method can provides a rapid analysis of shale samples and can potentially benefit the depleted gas shale carbon sequestration

Physics of LIBS

Atoms and ions emit light at specific wavelengths and frequencies. With this unique correlation, it has been possible to use spectra as finger print of emitting species. Plasma is generated by focusing laser pulse on a surface and subsequently vaporization, atomization and excitation follows. The resulting plasma which is a neutral mixture of electrons, ions and molecules is suitable for qualitative analysis (identification of elements) and quantitative analysis (sample composition through calibration curves). Temporally and spatially resolved plasma provides great advantages over other standard analytical techniques. It prepares and excites the sample in single step. LIBS can be operated in harsh and difficult environmental conditions.

Experimental/ Sample preparation

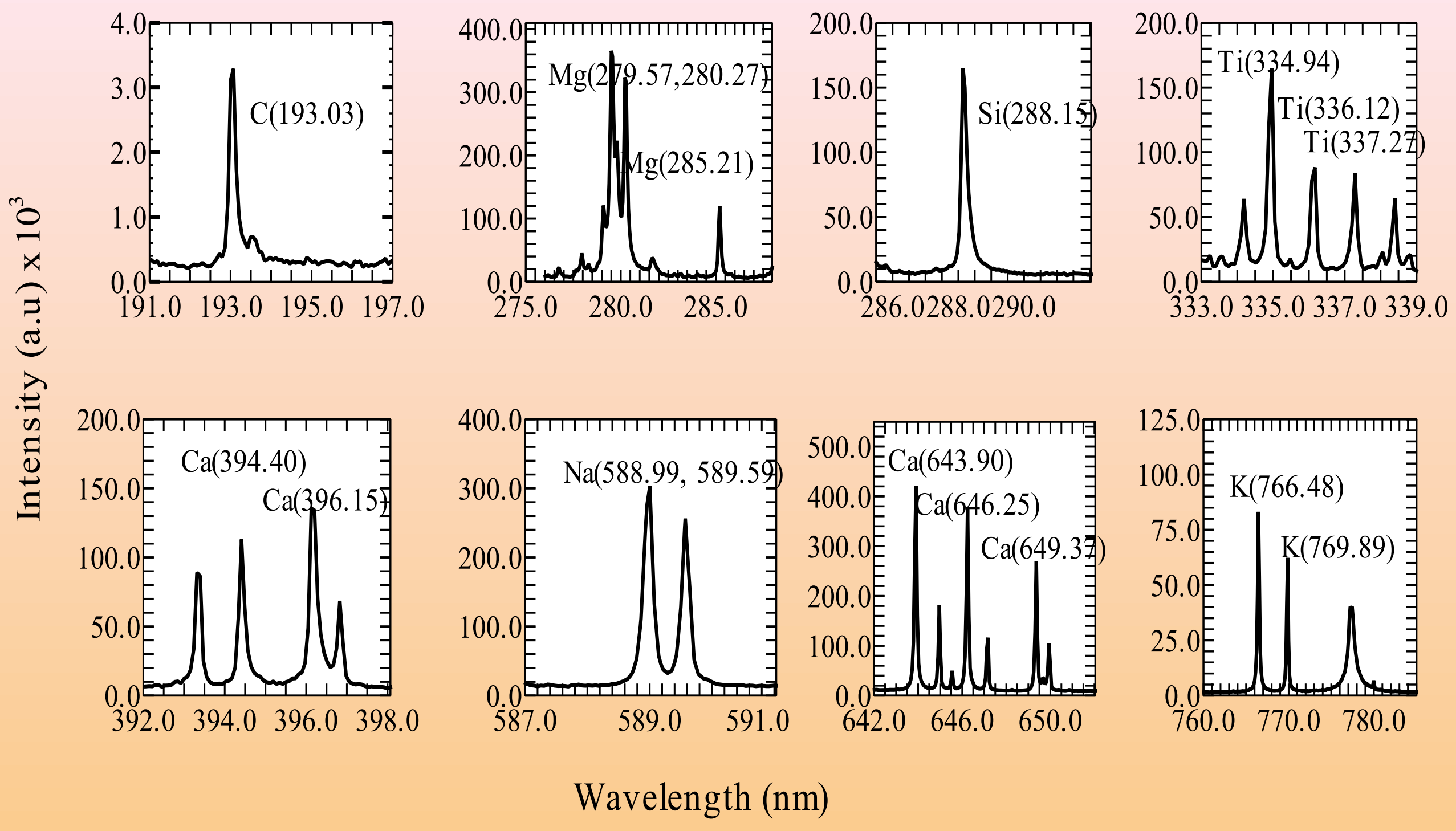
Ten outcrop samples from Marcellus Shale (Reference) were used in this study. The powdered samples were pelletized into ten pellets with a diameter 13 mm by approximately 8-ton pressure during 4 min of dwell time and 2 min of release time. No binder was added to the pellets.

Measurements were performed using a J200-EC LIBS instrument (Applied Spectra, Fremont, CA) configured with a 266-nm ablation laser and a 6-channel optical spectrometer coupled to gated CCD arrays for broadband spectral registration within 190–1040 nm at resolution of about 0.1 nm. Laser pulse energy was 25 mJ, a pulse duration was approximately 4 ns, while a flat-top shaped laser beam was collimated onto the sample to an ablation spot of 150 µm in diameter. Laser pulse repetition frequency was 10 Hz. An optimal gate delay for sensitive acquisition of both atomic and ionic lines of elements was selected as 0.2 µs. A gate width was fixed at 1.05 ms. All measurements were performed in air at atmospheric pressure.

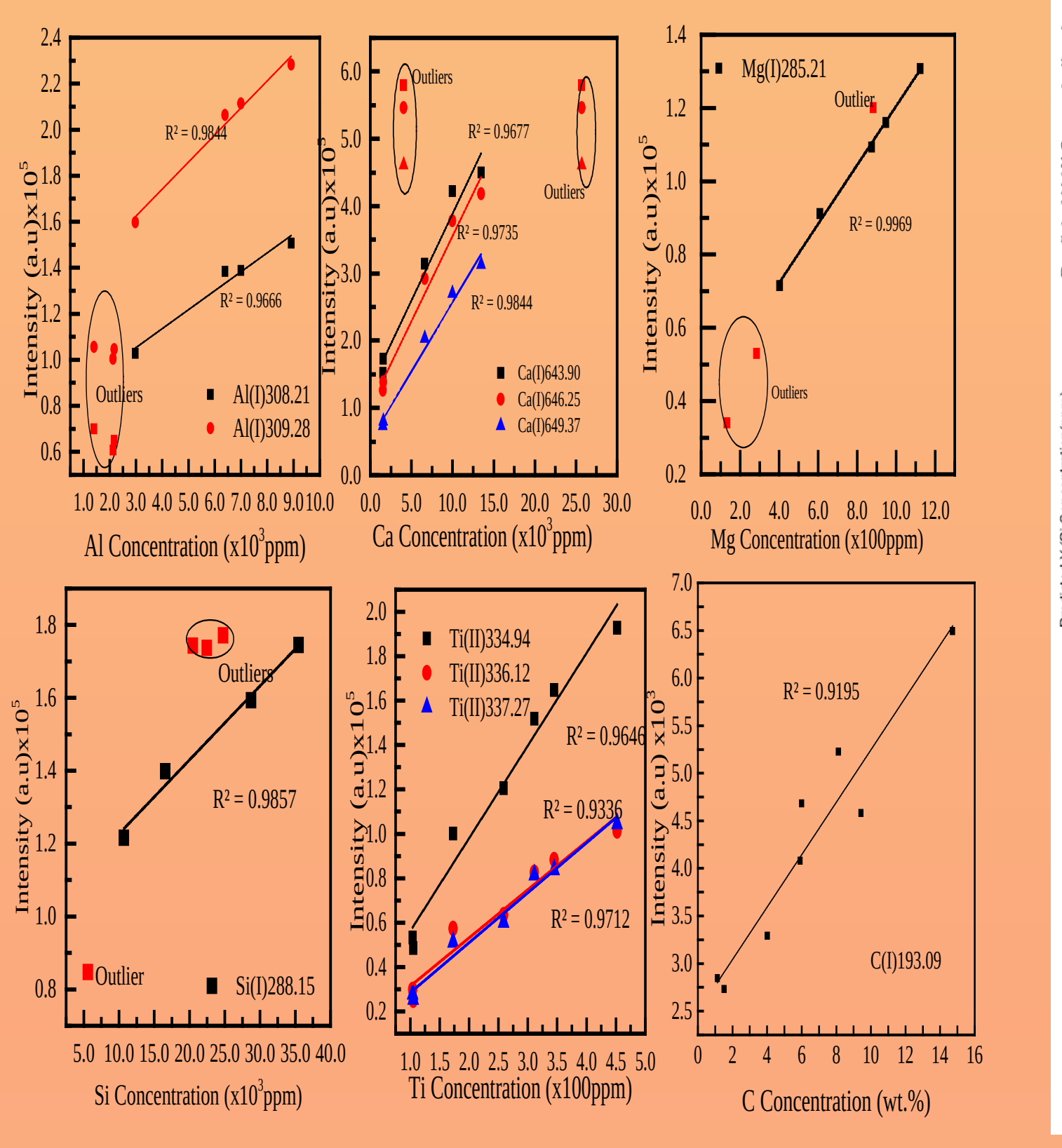
The samples were interrogated using a grid of 7×7 laser ablation spots, covering an overall area of 1.9×1.9 mm^2 on the surface of every pellet. Each spot of the grid was ablated with 10 laser pulses and the spectra acquired from these 10 pulses were accumulated. As a result of this interrogation, 49 individual spectra were collected from each sample. These spectra were used to build a multivariate partial least squares model, which rectified inter-sample differences while retaining inherent variability of the LIBS signal within every sample.

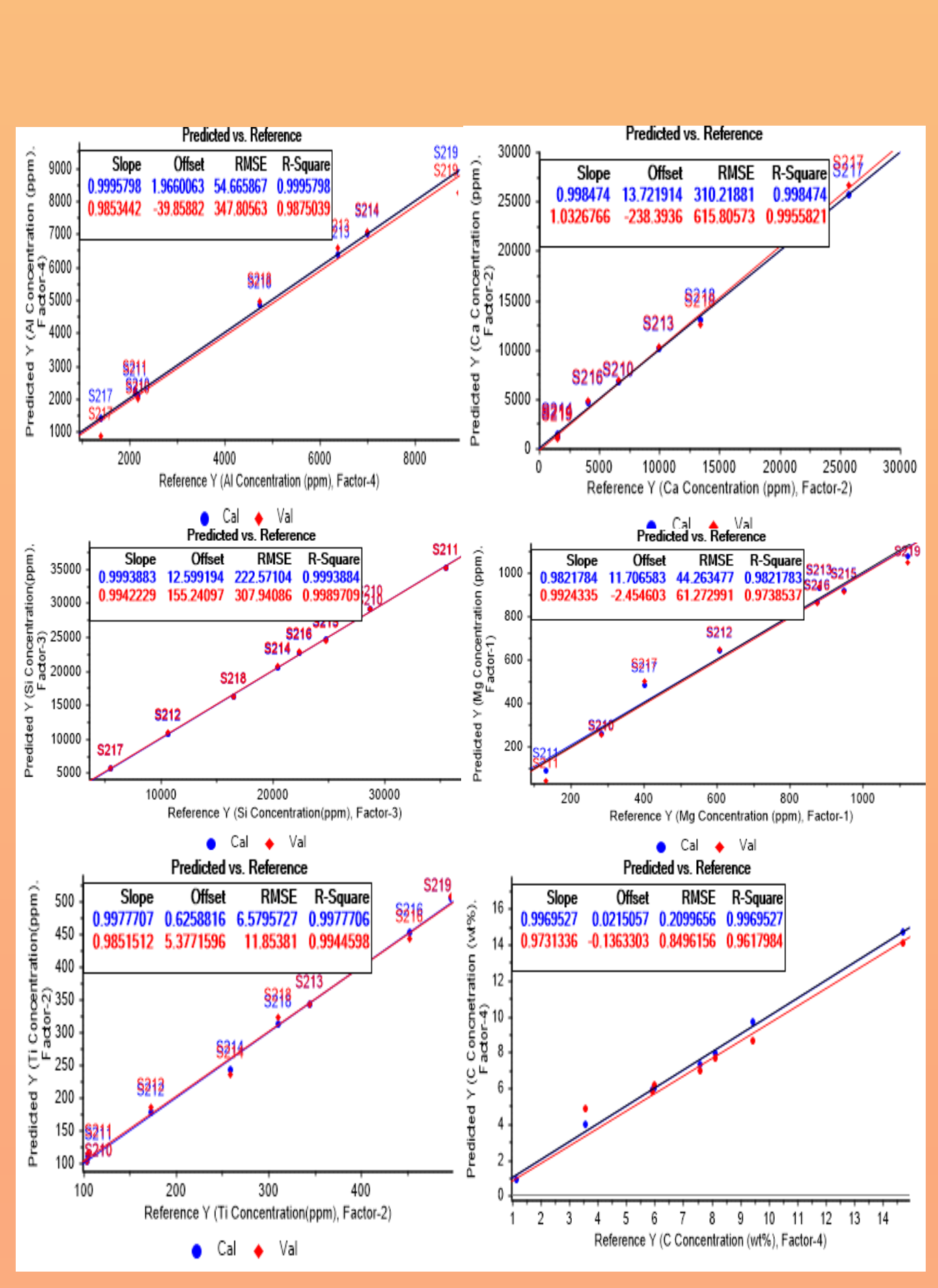
Qualitative Analysis

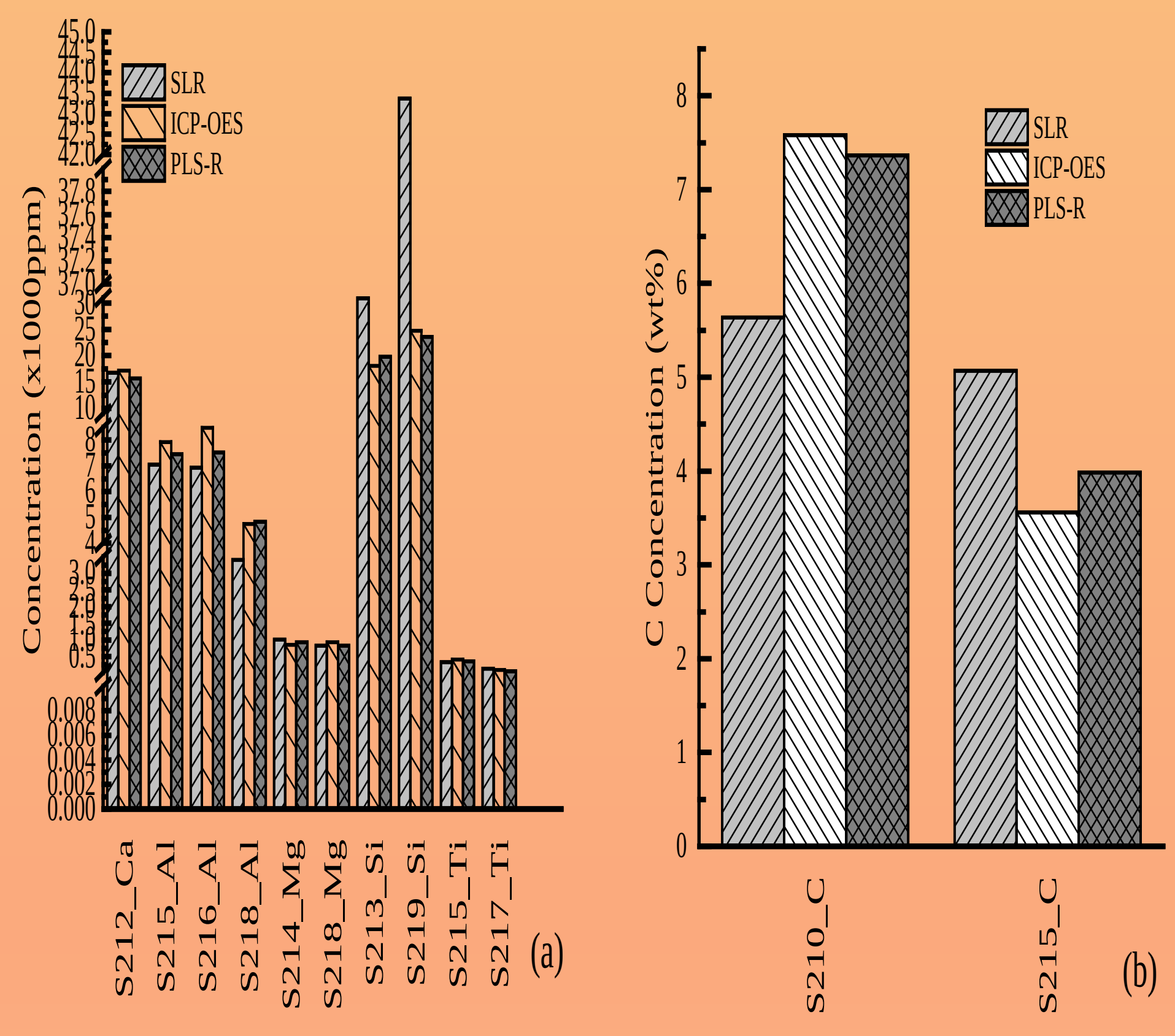
Qualitative analysis was performed for major elements in shale rock notably Mg, Si, Ti, Ca, Na, and K. Spectral line of carbon was also detected. Spectra plotted herein were resolved with respect to Signal-to-noise and signal-to-background ratios.



Quantitative Analysis







Results and discussion

With the resolved LIBS spectra, we could quantitatively analyze Al, Ca, Mg, Si, Ti and C. Outliers are observed in the univariate (SLR) calibration curves. This could be due to the shot to shot fluctuations of the laser energy. A high accuracy error is also noted with SLR prediction of Si. This can be attributed to the silicate nature of shale rocks. Silicate rocks in fact present a high matrix effect of Si which interferes with Ti. The results are improved using multivariate analysis such as Principal least square (PLS-R) in order to take into account the strong matrix effect. PLS-R also increases the linear dynamic range of the concentration.

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