Application of Laser Induced Breakdown Spectroscopy (LIBS) in analysis of groundwater and outcrop samples from the Marcellus shale

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Abstract

Organic rich shale formations are unique in the production of natural gas because those not only serve as a source for the gas but also form the reservoir. In addition, the formations that are depleted of the gas are potential candidates for geologic storage of CO_2 accompanied by an enhanced gas recovery (EGR). Both CO_2 and natural gas adsorption/desorption seem to have a correlation with mineral composition of the shale rocks. Also the rocks that contain higher amount of organic material have greater ability to generate natural gas and potentially a greater capacity of CO_2 storage. In order to ascertain the utility of laser induced breakdown spectroscopy (LIBS) for elemental characterization of shale rocks we analyzed the outcrop samples from the Marcellus Shale. It is advantageous to use LIBS because it enables a rapid in situ sample analysis with little or no sample preparation and can perform multi-element analysis including total carbon. In this study, a powdered sample was pressed to form a pellet and used for LIBS analysis. Laser pulse energy 25 mJ, a pulse duration 4 ns, gate width 1.05 ms, and gate delay 0.2 µs were used and the data were collected using 10 laser shots per spot of 150 µm diameter. Between partial least squares regression (PLS-R) and simple linear regression (SLR) calibration methods the PLS-R yielded better accuracy error. The samples were also analyzed using ICP-OES and a comparison between LIBS and ICP-OES results showed that the both results were comparable within $\pm$ 10%. Use of LIBS to assess groundwater quality due to subsurface activities will also be discussed. Development of a LIBS method would provide rapid analysis of shale samples and would potentially benefit the depleted gas shale carbon sequestration research.

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.

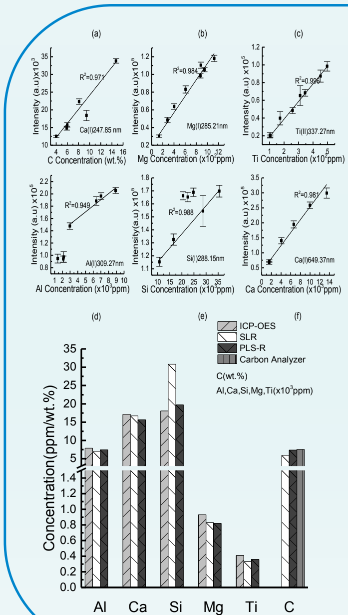
Measurements were performed using a J200-EC LIBS instrument (Applied Spectra, Fremont, CA) configured with a 266-nm ablation laser and a 6-channel optical spectrometer coupled to gated CCD arrays for broadband spectral registration within 190–1040 nm at resolution of about 0.1 nm. Laser pulse energy 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.

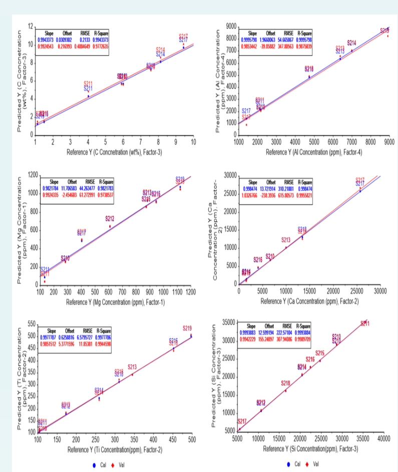
The samples were interrogated using a grid of 7×7 laser ablation spots, covering an overall area of 1.9×1.9 mm^2 on the surface of every pellet. Each spot of the grid was ablated with 10 laser pulses and the spectra acquired from these 10 pulses were accumulated. As a result of this interrogation, 49 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, Ca 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





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 emission line fluctuation as a result of the laser energy instability. 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 interfere with Ti. The results are improved using multivariate analysis such as Principal least square (PLS) 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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