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Rapid Determination of Bitumen Content in Athabasca Oil Sands by Laser-Induced Breakdown Spectroscopy

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ABSTRACT: Evaluation of bitumen content in oil sands feedstock is important to control the extraction process and improve the recovery efficiency. Current standard techniques for bitumen determination in oil sands ore suffer whether from their time-consuming labor intensive method of sample preparations or from requiring a high number of samples for calibration purposes. The analysis of bitumen ore samples is very challenging for the analytical chemist due to its nature of several phases of wet and dry particles and heterogeneous mixture of clay, bitumen, water, and solid contents. In this paper, we present a new enabling method using LIBS to determine rapidly and without sample preparation the bitumen content in oil sands ores. A qualitative study by principal component analysis was first done, and then a partial least-squares method was performed to assess the feasibility of determining bitumen by LIBS. The results show a good correlation between LIBS spectra and bitumen content and a prediction averaged absolute error around 0.7%. This method demonstrates that the LIBS is a promising tool for rapidly assessing oil sands ore grades either in the lab, at-line, or online. Elemental composition of solids is also investigated.

■ INTRODUCTION

The Athabasca oil sands (Canada) are considered to be the largest oil sand reserves in the world.¹ Oil sands are heterogeneous mixtures composed of about 4–18% of bitumen, about 55–80% of mineral solids including coarse sand, silt, and clay, and about 2–15% of water.² Oil produced from oil sands by surface mining methods involves the basic steps of mining the oil sands, slurry phases for separation, bitumen recovery by flotation, upgrading for synthetic oil, and finally refining. Prior to the recovery of bitumen by flotation, it is important to characterize the oil sands feedstock ore content to optimize the process and make a decision on recovery efficiency and economic value perspectives. These measurements can be done in the laboratory or on an apron feeder to monitor the feedstock. However, current methods for assessing oil sands content are time-consuming and labor intensive as well as difficult to control due to the complexity and heterogeneity of the samples that contain different particle sizes and several components. The industry standard for determining bitumen, water, and solids contents of oil sands ore samples is the Dean–Stark extraction method.³ Full extraction of bitumen from the solids takes several hours to complete. Once the three components have been separated, the clean and dry solids can be quantified by a variety of techniques, including elemental analysis by inductively coupled plasma (ICP) or X-ray fluorescence (XRF), and mineralogy by X-ray diffraction (XRD). The Dean–Stark extraction method requires large amounts of expensive solvents and suffers from time-consuming labor intensive method of sample preparations. Low field nuclear magnetic resonance (NMR) spectroscopy has also been used for measuring bitumen and water.⁴ Although that solid content can be determined by the difference between the total content and the water and bitumen contents, the technique cannot give atomic elemental and mineralogical information. Near-infrared reflectance (NIR) measurements between 800 and 2500 nm have been used to estimate the bitumen content

since the early 1990s.^{5,6} Despite substantial efforts to improve reliability and robustness of NIR analyzers, the technique still requires a huge number of samples for calibration purposes while providing only information on bitumen content. Due to these difficulties mentioned above, there is a need in the oil sand industry for a breakthrough technology able to determine the content of bitumen quickly and without sample preparation in the laboratory or online.

Laser-induced breakdown spectroscopy (LIBS) appears to be a potential candidate technique to fulfill the requirements of the oil sands industry. The technique has already been used to characterize other types of mining and geological materials^{7–9} as well as to monitor mineral processings.^{10,11} LIBS is a spectroscopic technique which uses a high power pulsed laser beam focused onto a sample to ablate a small quantity of materials from the sample surface, typically a few nanograms, and create a hot temperature plasma where atoms and ions are in the excited state. As the plasma cools, the atoms and ions return to their fundamental states by emitting radiation. This emitted radiation is detected by a spectrometer. Wavelengths of either atomic transitions or molecular bands¹² provide qualitative information on the chemical composition of the ablated material, and the spectral intensities are related to the content concentrations. In addition to the ability to measure simultaneously several atomic elements, LIBS can measure light elements ($Z < 12$) such as carbon, hydrogen, oxygen, etc., unlike XRF. Studies on shale^{13,14} and coal^{15,16} demonstrate that LIBS may be used to measure the organic components of natural samples. Moreover, the development of spectral analysis tools such as chemometrics^{17–19} makes the LIBS spectroscopy a more powerful tool for quantitative measurements.^{20,21} All of

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these features make LIBS an excellent candidate to characterize the oil sands composition. To the best of our knowledge, no study exists on the determination of bitumen content in oil sands ores using LIBS.

This paper presents a new application of LIBS for characterizing oil sands ores. In this paper, we present a new enabling method addressing the challenges of analyzing oil sands by LIBS in order to determine the bitumen content without sample preparation. Then the scattering of data points due to the heterogeneity as well as the solid composition is discussed.

EXPERIMENTAL METHODS

Representative 10 oil sands samples provided by a major oil sands company were used in this study. The texture of the samples varies from fine to coarse. Bitumen, water, and solid contents were determined by Dean–Stark extraction. Before analysis, the samples were kept and contained in a sealed bag in a freezer to avoid evaporation and keep their content of water. Three samples, not used in the quantitative calibration model, were used as a blind sample set. The blind method is more representative than the cross-validation one because the sample set is not seen by the model. The composition of these samples is summarized in Table 1. Laboratory LIBS measure-

Table 1. Composition of the Samples Analyzed by LIBS

	bitumen (%)	solids (%)	water (%)
sample 1	5.4	86.6	8.1
sample 2	2.7	90.4	6.6
sample 3	11.8	86.6	1.4
sample 4	10	84.1	5.8
sample 5	7.8	86.7	5.2
sample 6	13.6	82.1	3.8
sample 7	12.4	85.4	1.9
sample 8	7.4	85.5	7.1
sample 9	14.5	85.3	2.8
sample 10	9.4	83.9	7.6

ments on the oil sands samples were performed. The LIBS setup is equipped with a pulsed Nd:YAG laser operating at the fundamental wavelength of 1064 nm, delivering pulses of 125 mJ energy and 10 ns duration at a repetition rate of 5 Hz. This setup includes a 2-channel CCD spectrometer system covering a 220–900 nm range. This spectrometer system was selected to match the requirements needed for detecting the major elements present in the oil sands solids. The optical configuration allows for plasma emission to be collected along the same path as the laser beam delivery, perpendicular to the sample surface, with the sample placed approximately 50 cm from the focusing lens. An argon flow gas was used to keep an inert controlled atmosphere and to avoid the contributions of atmospheric air to the collected spectra. A sample holder was positioned on a 3-axis translational stage to laser scan the material surface. To achieve acceptable levels of representativeness of the measured material and accuracy of the acquired data, 1000 laser shots were made on a 5 × 5 mm² surface. To obtain a representative spectrum, measurements of the acquired 1000 spectra in each crater are averaged. Five replicates were carried out on each sample to evaluate the repeatability.

RESULTS AND DISCUSSION

The averaged representative spectrum for all the materials studied is presented in Figure 1. The main LIBS emission lines of oil sands are summarized in Table 2. As shown, C, Ca, Fe, H, Mg, Al, Ti, Si, Li, K, Na, N, and O were found in all materials. Molecular bands corresponding to C₂ and CN were also detected in all materials.

In order to emphasize the differences observed in different materials, a study of such a complex material requires chemometrics methods to extract the relevant information. Qualitative analysis using principal component analysis (PCA)²² was first performed to identify significant information for each studied component in the oil sands. A quantitative model was afterward built using a partial least-squares regression (PLS)²³ method. Both PCA and PLS regression were performed using the commercial software SIMCA (Umetrics). PCA is an unsupervised multivariate method used for data reduction in uncorrelated variables called principal components. It decomposes a data matrix of averaged LIBS spectra for all the samples into two smaller matrices of scores and loadings, which were used here to find the correlation between the samples spectra. To reduce contributions of noise and background, only relevant wavelengths which are connected to the main major chemical elements in oil sands ores are selected. PCA was carried out on 50 averaged spectra, i.e., 10 samples and 5 replicates of each sample. LIBS spectra were normalized to reduce the signal intensity fluctuations by using the standard normal variate (SNV) method,²⁴ then reduced to 46 lines related to the most relevant chemical elements in Athabasca oil sands.²⁵

Figure 2 shows a PCA plot over 50 data points. The first component represents 69.5% of the variance, whereas the second represents 13.9%. The high values of scores on the first principal component correspond to high bitumen content, which is observed for samples 3, 6, 7, 9, and 10. In the reverse, the negative values of scores on the first component correspond to low bitumen content for samples 1, 2, 5, and 8. In order to understand the spectral origin of each principal component, loadings are plotted. Figure 3 shows the first two principal component loadings plot. The positive loadings reflect the LIBS lines of C and molecular bands C₂ and CN. This indicates that C, CN, and C₂ are correlated with the bitumen content and changes in the intensity of these LIBS lines have a strong effect on the bitumen content. Since C, C₂, and CN are commonly present in petroleum products, we can attribute those features to the bitumen presence in the oil sands material. Therefore, the correlation between the intensities of those lines in the loading spectra and the bitumen content in oil sands can be used for the quantification of the bitumen. To create a PLS model relating the spectrum intensity amplitudes to the bitumen content, 7 oil sands samples were used for model calibration and cross-validation. Cross-validation of the model was performed with the leave-one-out method. Three samples were used as a blind data set to evaluate the model performance.

The SNV method was used for the spectra pretreatment, and the same LIBS lines selected for the PCA were used as inputs. Figure 4 shows the PLS regression model between the measured bitumen content and predicted bitumen from LIBS spectra. Despite the limited number of samples, the correlation coefficient of calibration and prediction were 0.96 and 0.95, respectively. The root-mean-square of calibration (RMSEC) and prediction (RMSEP) are 0.79% and 0.66%, respectively. The variability of replicates was also estimated. The average absolute standard deviation for all of the samples was 0.65%. This preliminary result shows the potential of using LIBS to determine the bitumen content quickly in oil sands.

Figure 2 also shows a high scattering of the replicates located in the positive scores of the first principal component compared to the samples located in the negative scores. This scattering is

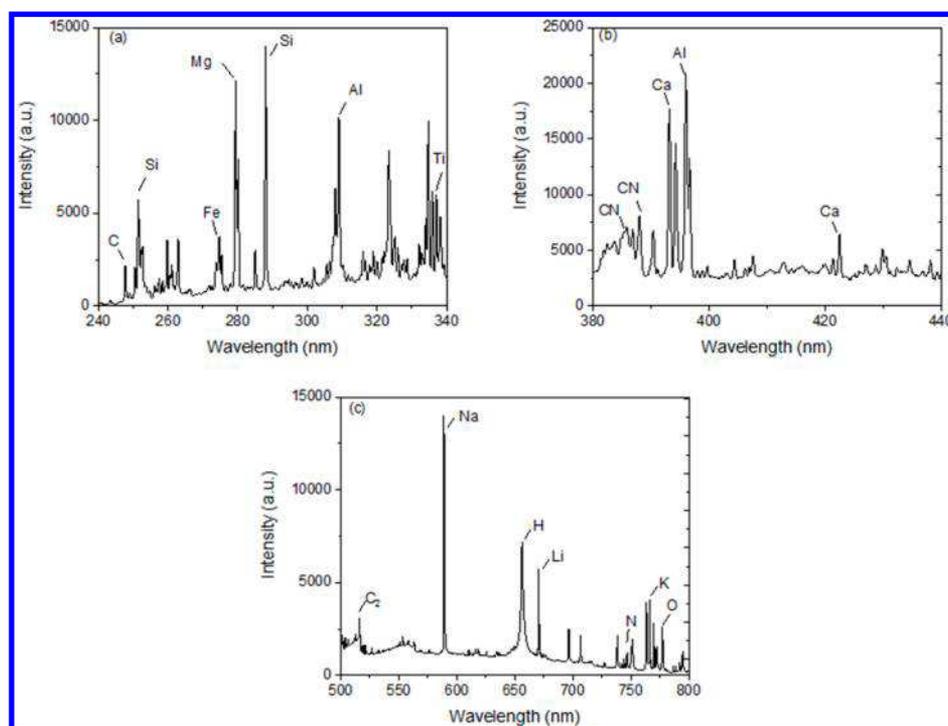


Figure 1. Averaged LIBS spectrum of all of the samples in different spectral ranges showing main emission lines and bands.

Table 2. Main Emission Lines and Bands Detected by LIBS^a

species	wavelength (nm)
C	247.86 (I)
C ₂	467.80, 469.27, 471.03, 512.90, 516.50
CN	384.91, 385.32, 386.03, 387.00, 388.12
Si	288.16 (I), 251.61 (I), 252.85 (I), 250.69 (I)
Al	309.27 (I), 394.40 (I), 396.15 (I)
Ca	315.88 (II), 393.36 (II), 396.89 (II), 422.67 (I), 430.25 (I), 616.72 (I)
Mg	279.55 (II), 280.27 (II), 285.21 (I)
Fe	273.95 (II), 274.65 (II), 275.01 (II)
Ti	332.29 (II), 332.94 (II), 334.84 (I), 334.94 (I)
K	766.48 (I), 769.86 (I)
Na	588.99 (I), 589.60 (I)
H	486.27, 656.28
O	777.19 (I), 777.41 (I), 777.54 (I)
N	746.8 (I), 821.63 (I)
Li	670.76 (I)

^a(I) or (II) refers to emission from neutral atoms or emission from singly ionized atoms, respectively.

due to the variation of the emitted optical signal over 5 replicates. Moreover, samples located at the right of the PCA scores plot are highly scattered along the second principal component. It is expected to observe such a scattering since oil sand is complex material and the solids type varies from sandy material with large grains size to fine material with small grains size. The heterogeneity of oil sands can even be seen with the naked eye: some oil sands samples exhibit grains of different sizes and colors. In addition, loadings in Figure 3 exhibit that the highest values in the vertical direction are sensitive to Si lines intensities. As quartz, which is a coarse material, is the major mineral of Athabasca oil sands, it is not surprising to observe sandy and coarse samples exhibiting more heterogeneity and therefore more emitted signal variation than like-

powder samples. Conversely, Figure 2 shows that the samples 1, 2, 4, 5, and 8 exhibit a small scattering along the second PC. The loadings reveal that these materials are correlated with Al, Ti, K, and Mg. Since bitumen and water contain trace amounts of minerals, Al, Ca, K, Mg, and Si lines can be attributed to solid minerals of oil sands, which are primarily quartz and clays. Mercier et al.²⁶ demonstrated that clay minerals such as kaolinite and illite have a negative impact on bitumen recovery. So having a tool that provides the elemental composition of oil sand solids can help to give information about the minerals variation in oil sands feedstock. As known, the minerals contained in Athabasca oil sands are primarily quartz sand (usually more than 60%). Si is the primary element in quartz; however, Si is also present in clays but at a lower concentration than in quartz. On the other hand, Al is the major atomic element present in clays. Oil sands ore may contain other minerals that comprise Al, such as albite or microcline, but at low concentration. Thus, Si and Al lines can be used to estimate the quartz and clays variability in oil feedstock. Another key element in oil sands is potassium. K is present in some oil sands clay such as mica and illite and can also be present in other minerals such as microcline which is a negligible mineral in oil sands ore. K is already used as a clay signature in the oil sands industry.²⁷ This work shows that the LIBS spectra coupled to PCA reveal a negative correlation in the loadings of Si and clay indicators Al and K, which indicates that Si content increase corresponds to K and Al contents decrease. Consequently, this could indicate when quartz content increases, clays content decreases, which is in accordance with the known behavior of oil sands mineralogy.

This preliminary result on solid composition exhibits the potential of assessing chemical elemental abundance by LIBS without removing bitumen. Providing such information is critical to evaluate the ore grade and therefore the bitumen recovery. So far, there is no technique that can provide both bitumen and elemental information. The ability of LIBS to

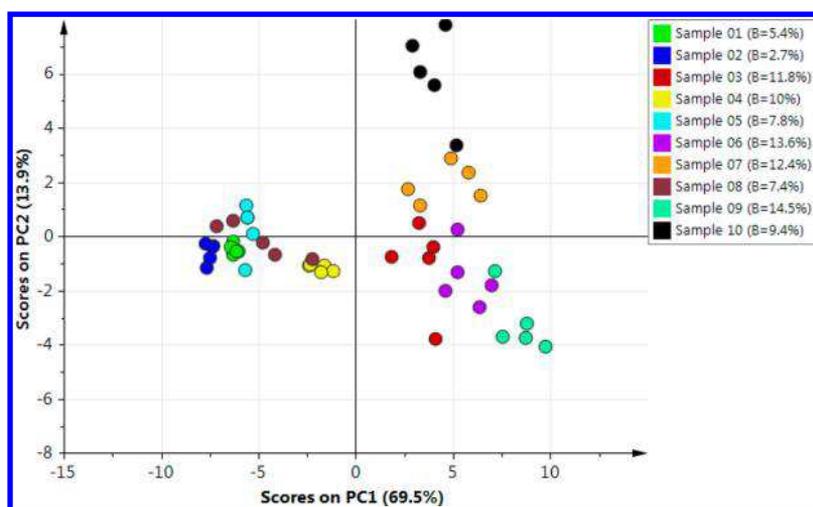


Figure 2. PCA score plot for LIBS spectra. The legend includes the bitumen content (%) in each sample.

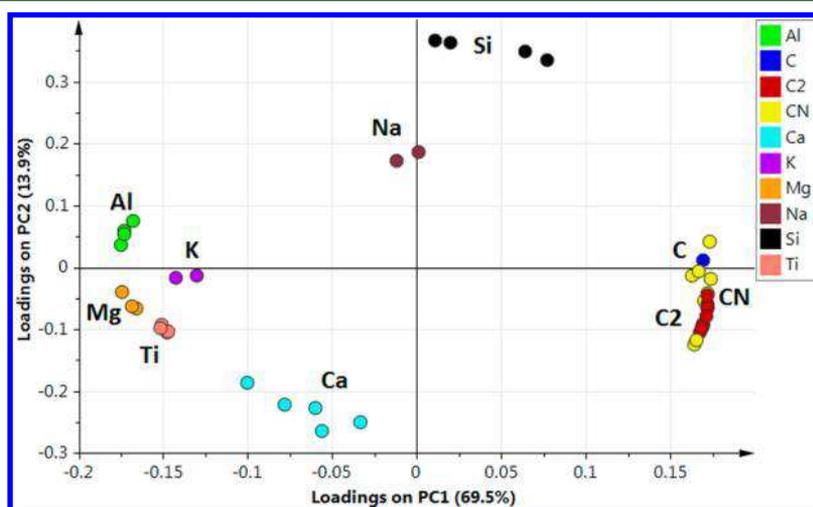


Figure 3. PCA loading plot of the first and the second components.

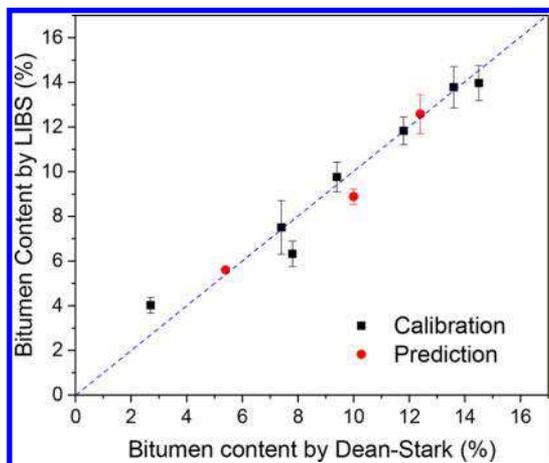


Figure 4. Comparison of bitumen content to values predicted from LIBS data. Dashed line represents 1:1 parity between reference and predicted values.

provide information about bitumen and key mineral elements from the same acquired spectra deserves to be investigated. For that, XRF and XRD measurements on samples with a wide variety of minerals are required to confirm this interpretation

and therefore the potential for using the LIBS spectra as a grade predictor.

CONCLUSION

This work investigated the application of LIBS to Athabasca oil sands samples to find a correlation between LIBS spectra and bitumen content. Results show the combination of LIBS and chemometrics proved to be a novel rapid quantitative method for assessing bitumen in oil sands without sample preparation and with only 7 calibration samples. The method represents a real alternative to traditional methods in the oil sands industry. Moreover, as the LIBS fingerprint is information-rich, this method could also provide additional information about elemental solid composition and therefore some key elements related to either clays or quartz signature evaluation. So several potential applications can be targeted such as monitoring the statistical variation of LIBS data of oil sands in real time at an apron feeder to evaluate the feedstock grade. Future work includes XRF and XRD analyses to validate the feasibility of the LIBS technique for minerals and clays estimation. More samples with wide mineralogical types and bitumen composition will be studied to investigate various sampling strategies and to improve the precision and the accuracy of bitumen prediction.

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Notes

The authors declare no competing financial interest.

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