

Rapid mineral detection using elemental Laser-Induced Breakdown Spectroscopy

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KEY WORDS: mineral interpretation, calibration, LIBS, SVD

ABSTRACT

The exploration and mining activities are strongly increasing both in Finland and internationally. During the exploration, rapid and on-line scanning of rock and drillcore samples gives fast results that can be used to ease the decision-making process for geologists and to guide the future drilling activities without delays. Traditional mineral exploration activities are moderately slow. Recently, faster and more efficient ore characterization by combining various laser-based and contactless measurement techniques have drawn tremendous attention in research. This combination will enable mineralogical analysis of the drillcore and recyclable materials in a fast, cost-effective and objective manner and provides complementary and partly substitutive information for the laboratory analyses. However, complexity of different measurement setups and the difference between the sources of light make it non-economic and complicated for industry. Laser-Induced Breakdown Spectroscopy is a very simple spectroscopic technique with reasonable level of competence to identify wide range of elements. It inspires the importance of applying LIBS for fast scanning purposes. This study proposes a simple statistical analysis technique leading to rapid mineral identification from the elemental results of LIBS. Moreover, application of LIBS technique for calibrating other fast surface scanning techniques like Laser-Induced Fluorescence imaging, functioning through similar measurement setup, will be presented.

1 INTRODUCTION

This study addresses the issue of rapidly finding and locating minerals from the surface of rock and drillcore samples using Laser-Induced Breakdown Spectroscopy (LIBS). LIBS is a well-known and widely applied elemental measurement technique. Prior knowledge about mineralogical contents of the rock and drillcore samples is essential for geologists and makes the process of logging more effective, thus saving time and manpower. X-ray Fluorescence (XRF) /1/ and reflectance spectroscopy in the visible and infrared ranges /2/ are the prevailing online surface scanning techniques in industry. However, XRF is an elemental technique and not appropriate when the target is to detect light elements (usually with atomic number less than 20). Furthermore, various elements may appear with similar characteristic emission lines which makes the decision-making process uncertain. Reflectance spectroscopy is also a widely applied online surface scanning technique, however there are still a number of mineral groups left unknown for reflectance spectroscopy. The wide range of the elements which can be detected by LIBS and the simplicity of the measurement setup provides enough motivation to apply LIBS for fast scanning purposes. The main challenge is to interpret the existing minerals from the

elemental contents provided by LIBS. Thereby, one major phase of this research is about mineral interpretation from the elemental contents using statistical methods.

Combining different contactless measurement techniques can lead to faster and better characterization of drill core samples and it has been investigated and proved in various research works. For example, it has been shown how LIBS technique provides complementary information for hyperspectral images /3/. Also, a combined LIF-imaging and Raman spectroscopy technique has been introduced as a reliable technique generating a mineral map from the surface of the drillcore samples /4/. It should be taken into account that the complexity of the laser setups and the difference between the sources of light makes it non-economic and complicated for industry. Since LIBS and Laser-Induced Fluorescence (LIF) techniques can apply the same source of light at similar wavelengths (UV range) and considering the simplicity of LIBS measurement setup, the combination of LIF and LIBS can be a favourable approach. This study concentrates on the topic of mineral detection using elemental results of the LIBS measurement technique. A method of data processing is demonstrated leading to application of LIBS technique as a capable method in order to calibrate and give complementary information to other surface scanning techniques.

2 Problem statement and objectives

For LIBS, a large number of analytical methods for data processing is available. Principal Component Analysis (PCA) is very commonly used for LIBS data processing. However, the analysis is still an ambiguous process and usually cannot be performed automatically (see the report of /5/). The peaks are translated using a reference database of atomic emission lines. The most regularly used database is the Atomic Line Database by The National Institute of Standards and Technology (NIST) /6/. The interpretation of the LIBS lines using reference database is usually performed indecisively and based on personal impressions since multiple elements may emit at similar lines. Moreover, the intensity of the emission lines can be affected by many factors such as the intensity of the laser light, the distance of the sample from the laser, the shape of the sample and other factors like the moisture or external lights. Therefore, such conventional analysis methods restrict LIBS technique for online and fast mineral or elemental identification purposes. Nonetheless, the ratios of the line intensities of the similar samples are usually constant /7/ and this fact is the key point of this research enabling fast mineral detection using LIBS results.

This work proposes a supervised learning algorithm resulting in online application of LIBS to mineral detection. In this work target minerals are studied in advance so that purred (or high-grade) minerals of interest are measured by LIBS technique. For each target mineral, average of multiple measured spectra is evaluated and the most representative and repetitive peaks are selected as the characteristic of the target mineral. Then, a database of minerals reference spectra is manually produced. Each new spectrum measured by LIBS is inserted into the algorithm alongside the reference spectra. Using a suitable statistical technique and a proper distance metric function, the reference spectrum most similar to the new measurement is identified. Accomplishment of this work demonstrates the feasibility of applying LIBS technique for rapid mineral detection.

3 Developing reference spectra

The reference spectra can be produced either manually by referring to a reference database of atomic emission lines or by direct measuring of high grade samples of interest. This section explains the procedure of building the

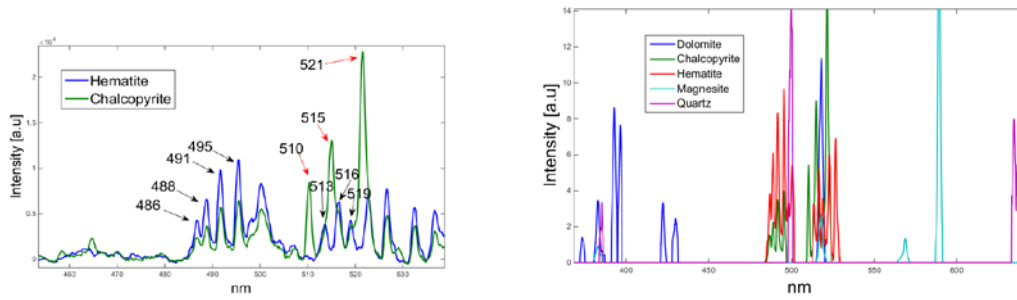


Figure 1. a) Important atomic transition lines selected as indicators for Hematite and Chalcopyrite. b) Generated reference spectra

reference spectra by direct measuring. The LIBS spectra are broad bands from 350 nm to 800 nm. Figure 1.a represents atomic transition lines selected as indicators for Hematite (Fe_2O_3) and Chalcopyrite (CuFeS_2) minerals. Both minerals have a number of similar transition lines (e.g. 486 nm, 488nm, 491 nm, 495 and etc.) due to having iron in common. However, the difference reveals at wavelengths such as 510 nm, 515 nm, 521 nm for Chalcopyrite and 513 nm, 516 nm and 519 nm for Hematite. Baseline correction has been performed using an asymmetric least squares smoothing algorithm (/8/) to highlight the peaks. A small wavelength range around each peak is selected and the rest are set to zero. Reference spectra of other desired minerals are produced similarly. Figure 1.b demonstrates the generated reference spectra of Dolomite, Chalcopyrite, Hematite, Magnesite and Quartz minerals. Each spectrum is normalized to unit variance. Expertise is required to select the proper peaks of the minerals. Selection of irrelevant peaks adds to the complexity and influences the accuracy of the results. For instance, it is essential to select emission lines of Copper (Cu) for Chalcopyrite (CuFeS_2) mineral. Otherwise, many Iron-bearing minerals will show characteristic spectrum similar to Chalcopyrite. The transition lines selected for reference spectra of five minerals are listed in Table 1. The intensity of the emission lines are in arbitrary unit. Intensity values of the reference spectra are considered as reference values for identification.

Table 1. Atomic transition lines used in this study as characteristics of the reference minerals

<i>Mineral</i>	<i>LIBS Lines (nm)</i>
Dolomite	374, 383, 393, 397, 422, 430, 518
Chalcopyrite	487, 489, 492, 495.5, 510.5, 515, 521.5
Magnesite	383, 385, 518, 568.5, 589
Quartz	385,390, 500, 634.5, 636.5
Hematite	487, 489, 492, 495.5, 500, 513.5, 516.5, 519, 522.5, 527

4 Analytical Approach

Suppose X denotes an $n \times m$ matrix where $n=k+1$, k corresponding to the number of reference spectra and m the number of wavelengths (variables). The last row of the matrix holds the new measured spectrum to be evaluated. When the problem is about fast or real-time identification of the minerals from LIBS spectra, it is very plausible that the number of samples is much less than the number of wavelengths, ($n < m$). Therefore, applying PCA and working with covariance matrix is very undesirable because of being very large and singular. Singular Value Decomposition (SVD) can be performed as an alternative for PCA especially when the number of samples is less than variables /9/. It decomposes the matrix X into:

$$X_{n \times m} = U_{n \times n} T_{n \times m} V_{m \times m}^t \quad (1)$$

The product of U and T contains the scores and V^t demonstrates the loading values. Generally, SVD is a powerful solution for least square problems of any rank or shape. The matrix of the score values, $U \times T$, represents the spectra in n dimensions (note: when $n < m$, only the first n columns of T are non-zero). Considering the number of reference spectra, dimensions can be further reduced to p. Dimensionality reduction mitigates the impact of the noise coming from measurement setup and environment. In this study, the first three principal component directions were sufficient to interpret the data, $p = 3$. Therefore, each LIBS spectrum can be represented as a point in a three-dimensional space. The next step is to realize whether the measured spectrum contains any of the target minerals. A threshold, t, is defined and the new measured point is tracked so that its p-dimensional Euclidean distance with other points is calculated and stored into vector d:

$$d_i = \sqrt{\sum_p (v_{i,p} - c_p)^2}, i = 1, \dots, k \text{ and } p = 1, 2, 3 \quad (2)$$

c is the point associated with the measured spectrum and v_i is the representative point of the i^{th} spectrum. Nearest neighbours of the point c satisfying the condition $d < t$ are selected as the existing minerals in the measured spectrum. It is important to note that one spectrum may contain more than one mineral. Therefore, there will be two or more neighbours with approximately similar distances from the target point.

5 LIBS measurement setup

The laser-induced plasma was created using an ULTRA 100 Q-switched Nd:YAG laser operating at 266 nm with 25 mJ/pulse and up to 20 pulses/s repetition rate. The pulse duration was 8 ns. An optical fibre used to collect the radiation from the plasma and the spectrum was obtained by a USB4000 Fiber Optic Spectrometer covering from 350 nm to 1000 nm. A trigger delay of 7 μ s was set to avoid continuum radiation. Another way to avoid continuum radiation is to detect the emission at a few millimetres above the sample as the plasma plume expands and cools down. Both methods were used to keep away from the continuum radiation.

6 Results

6.1 LIBS for calibrating other techniques

A combined Laser-Induced Fluorescence and Raman spectroscopy method for mineral identification has been introduced by /4/ and the viability of the approach has been deeply discussed. However, there are still a number of important minerals non-responsive with both LIF-imaging and Raman spectroscopy techniques. For example, important sulphides like Chalcopyrite and Pentlandite or iron-bearing minerals like Hematite are neither fluorescent nor easily traceable by Raman spectroscopy. Using the proposed analytical approach for LIBS mineral identification, this work demonstrates rapid identification of Chalcopyrite, Hematite and Quartz minerals from the surface of the rock and drillcore samples. Figure 2-a is showing an ordinary close-up photograph of one piece of the drillcore sample from the depth of 18 m collected from Kevitsa mine, Finland. Figure 2-b represents

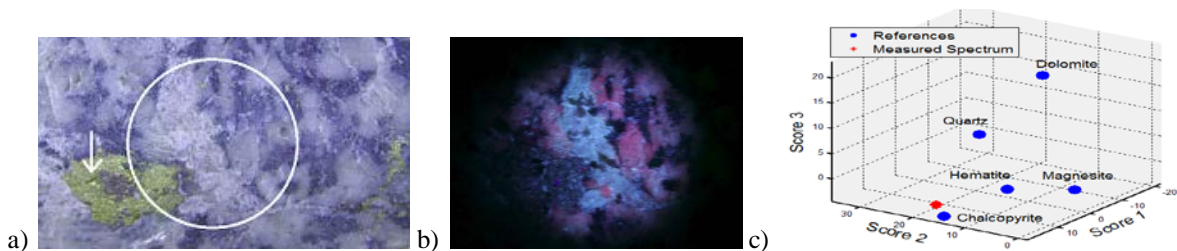


Figure 2. a) Drillcore from Kevitsa mine, depth 18 m. b) LIF image of the surface c) Scatter plot of the first three scores. Chalcopyrite is the nearest neighbour.

Laser-induced Fluorescence (LIF) image of the specified region in Figure 2.a (white circle) on the surface of the drillcore. LIF imaging was performed using the same YAG laser source utilized for LIBS technique (Figure 2.b). The red fluorescent colour is Albite and the bluish-white colour is Magnesite. However, in figure 2-a the golden colour spot (highlighted by arrow) did not fluoresce and was not identified by Raman spectroscopy. The position of the golden colour was measured by 10 pulses of LIBS. The analysis was performed to mimic the online or real time analysis of each new pulse. After baseline correction and scaling to unit variance, the average of the measured spectra was appended to the matrix of the reference spectra. Using SVD and the first three principal components, data were analysed in a new 3-D space. Figure 2.c shows the scatter plot of the first three scores where each data point stands for a full spectrum in the original space. The red point corresponds to the averaged spectrum measured from the golden spot on the surface of the drillcore. The Euclidean distance of the red point and the rest of the points was calculated. A threshold of $t=10$ was defined to recognize possible candidate minerals. The distance between the average of the measured spectra and Chalcopyrite was less than ten. Therefore, it can be deduced that the golden spot represents Chalcopyrite mineral. The proposed analytical method implies the feasibility of applying LIBS technique for rapid calibration of other surface scanning methods specially those functioning based on image processing of the drillcore surface.

6.2 Multiple mineral detection when mineral grains are mixed

When the laser beam hits more than one mineral grain at the same time, the spectrum holds a mixture of multiple lines of minerals. Numerous analytical methods applied to online mineral detection processes are incapable of identifying such spectra. Here we discuss the capability of the proposed method for identification of more than one mineral in a spectrum. Figure 3.a represents one piece of high-grade (> 60%) Hematite drillcore sample from the depth of 168 m below the ground level. The dark-grey, brownish and white colour veins represent high-level Hematite, low-level Hematite and Quartz respectively. The white arrow in Figure 3.a points to the position where Hematite and Quartz grains are mixed. In three-dimensional Euclidean space (Figure 3.b), the distance between the measured spectrum and Dolomite, Chalcopyrite, Hematite, Magnesite and Quartz were 18.4, 16.03, 6.8, 39.29 and 8.47 respectively. Figure 3.c illustrates the spectrum measured from the position specified by white arrow in Figure 3.a along with Hematite and Quartz reference spectra. Double-arrows indicate the wavelength range where measured spectrum is following Hematite and the single arrows represent the wavelengths where peaks of Quartz occur. Although the measured spectrum contains peaks compatible with other reference minerals, the variations of the data and the ratio of the peaks are mostly compatible with Hematite and Quartz. This sentiment is authenticated in figure 3.b where both Hematite and Quartz minerals situate in the close neighbourhood of the measured spectrum (red point) in the new 3-D space. Future research will focus on reporting the fast abundance estimation from large volumes of the samples. The proposed analytical approach will be extended to measure the concentration of the minerals and it provides the backbone of the future work.

7 Conclusion

This paper presented an analytical method leading to rapid mineral identification from the elemental contents of the LIBS technique. Using a statistical method (SVD), the minerals content of each spectrum measured by LIBS technique was evaluated. This evaluation was performed to imitate online and rapid mineral identification.

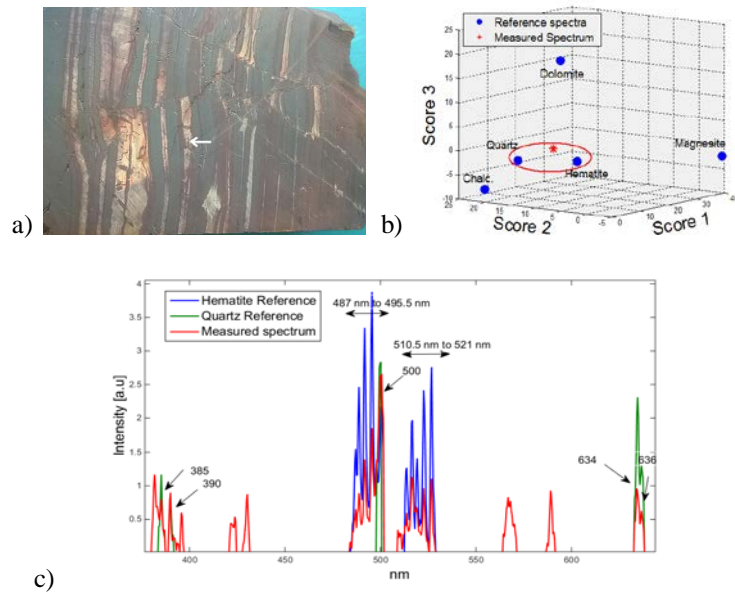


Figure 3. a) High grade Hematite sample b) Scatter plot of the first three scores. c) Measured spectrum and two reference spectra

Analysis was performed in a reduced dimension of the rotated space of the data points. A similarity search procedure was performed between the averaged spectrum of each measured position and the reference spectra produced manually. The results show that the proposed method can give complementary information to other surface scanning techniques like LIF-imaging. The feasibility of detecting multiple minerals in one spectrum was presented.

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