Libs-PCA based discrimination of Malaysian coins

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Abstract. The investigations of currency coins dated back to many centuries. Many researchers developed an interest in the investigation of the coin’s weight, size, physical feature and elemental composition. Laser-induced breakdown spectroscopy (LIBS) has the novelty of analytical analyses of various samples. It has the ability for the elemental composition determination of samples of solid (including metals), liquid and/or gases. Malaysia as a country uses Ringgit as a currency, among which are coins of 10, 20 and 50 cents. These coins are in series of release from the Malaysian Central Bank from time to time. There are currently in circulation old and new coins of 5, 10, 20 and 50 cents coins. These coins differ in their physical features and are may be different also in their elemental composition. This paper presents the investigation of the differences in elemental composition between the old and new Malaysian coins of 10, 20 and 50 cents. Principal component analysis (PCA) was used to perform the discrimination between the coins from the LIBS spectra.

1. Introduction
Laser-induced breakdown spectroscopy (LIBS), also known as laser-induced plasma spectroscopy (LIPS), is one of the common and widely used analytical techniques based on optical emission spectroscopy [1, 2], it is an excellent, convenient and less-expensive analytical technique [3]. LIBS was first introduced in the 1960s as an elemental analytical technique [4], and became popular after the development of sophisticated detectors and spectrometers [5]. The technique was first developed for specific applications in the laboratories, but it was available for general applications in 1990s. It was not until 1990s that LIBS found attention in general applications [6]. When a laser beam is focused on the surface of a sample, some amount of the material is ablated, vaporized and ionized to form a plasma plume with a spectral light having a characteristic of the material’s elemental composition [7]. The knowledge of the sample ablation, plasma formation and optical emission spectroscopy has brought about advancement in analytical science and techniques, resulting in fast and robust method of identification, classification and discrimination of various samples of a wide variety of materials. This combined technique is known as the laser-induced breakdown spectroscopy (LIBS) [8]. LIBS has been applied successfully for the samples characterization [9], dynamics [10],
classification and discrimination of different samples, including soil [11], leaves [12], rocks and soils [13], alloys [14], polymer [15], etc. The type of spectrometer to be used in LIBS elemental analyses requires a balance among the spectral resolution, wavelength, time, limit of detection (LOD) and the dynamic range [16].

LIBS integrated with rain forest (RF), out-of-bag (OOB) estimation, cross-validation (CV), partial squares discriminant analysis (PLS-DA) and support vector machines (SVM) was developed and applied for the discrimination and identification of nine steel grades in [17]. Costa et al [15] proposed a rapid measurement technique using LIBS and classification models such as k-nearest neighbors (KNN) and soft independent modelling of class analogy (SIMCA) to rank polymers. Campanella et al [18] recently used LIBS spectra based on artificial neural networks for the classification of aluminum alloys. The classification was done based on simple emission line ratios. Principal component analysis (PCA) algorithm for feature extraction and multilayer perceptron algorithms and neural networks were applied for classification of laser-induced breakdown spectroscopic data of four proteins: Bovine Serum Albumin, Osteopontin, Leptin and Insulin-like Growth Factor II was studied in [19].

Principal component analysis (PCA) is one of the powerful techniques in chemometrics. PCA is sometimes complemented by an algorithm to get the required classification [20]. LIBS has the capability to distinguish between different materials, even if the difference between the composition elements is minute [21]. Unnikrishnan et al [22] applied 3rd harmonic (355 nm) nanosecond pulse from an Nd:YAG laser to create plasma on the sample surface of plastic and identified the type of the plastic from the plasma emission. Principal Component Analysis (PCA) of the LIBS spectra was employed for the classification of the plastics. Vitkova et al [23] applied the combination of principal components analyses (PCA) and linear discriminant analyses (LDA) on LIBS spectra with multivariate statistical methods for comparative classification of brick samples. LIBS were used to classify the 29 brick samples from 7 different locations. Stand-off and table-top set-ups were used to compare the obtained results. All these studies prove the capability of the LIBS technique for classification of a variety of samples, no matter how little their difference may be.

Investigation of coins has over the years generated interest among many researchers, there is high interest in classification of these coins to originals or copies, old or new. There is challenge in explaining the weight, physical features, composition [24] or even the size of the coins. Other methods such as x-ray fluorescence (XRF) [25, 26], scanning electron microscope (SEM) [27] etc. have been applied for coins analyses. Investigations of the differences in the currency coins allow to obtain information on their elemental composition. LIBS has the ability to perform the differentiation, discrimination and identification of coins. This study is intended to study the differences in physical features and elemental compositions of old and new Malaysian coins (50, 20 and 10 cents) using the LIBS technique.

2. Experimental Setup

The schematic illustration of experimental setup used in this study is presented in Figure 1. A Q-Switched Nd:YAG laser (1064 nm, 6 ns, 650 mJ, 10 Hz) was focused onto the sample surface using a converging lens. Focused laser created a plasma plume on the sample surface, radiations emitted by the excited plasma species were collected by fiber optic cable aligned at 45° to the normal. Radiations were turned into spectrum by a 7-channel spectrometer (OceanOptics LIBS2500+). Gate delay and exposure times were kept constant during LIBS measurements at 3.75 µs and 1 µs respectively. Each sample (old and new coins of 10 cents, 20 cents and 50 cents) was exposed to 5 cleaning shots and 10 measurement shots at 10 different spots on the surface. In this way, 100 LIBS spectra were recorded for each coin.
Datasets to perform Principal Component Analysis (PCA) based discrimination on old and new sets of coins, set of old coins only and set of new coins only. Each set contained equal numbers of spectra for each set of coins. PCA was performed to discriminate among old coins of different values (i.e., 10, 20 and 50 cents).

3. Results and Discussion
Principal component analysis is dimension-reduction tool that reduces a large data to a small set still retaining most of its prominent features. It transforms a number of large number of possibly correlated variables into a smaller number of uncorrelated variables, which are termed as “principal components (PCs)”. Most variability of the data is contained by the first principal component; successive components carry as much of the remaining variability of the data. Scores of PCs can be plotted for a three-dimensional view of the data variance.

In this experiment old and new sets of coins 10, 20 and 50 cents of Malaysian currency are subjected to Laser induced breakdown spectroscopy and PCA is performed on their LIBS spectra. PCA brings out discriminatory information in terms of PC scores. In general, first few scores (2 or 3) contain more than 90% variance of a dataset. Therefore, a scatter plot of PC scores gives a pretty clear idea on how distinct are LIBS spectra of materials belonging to different classes.

3.1 Old (second) Series Coins
Looking at the elemental composition of old coins; same elements for 50, 20 and 10 cents (copper-nickel), we assume LIBS will not be able to discriminate between them. Figure 2 shows the images of the old coins while Table 1 illustrates the composition of both the new and old coins.
Table 1. Details of the elemental compositions of old (second) series and new (third) series of Malaysian coins.

| Coin Series | 50 Cents | 20 Cents | 10 Cents |
|-------------|----------|----------|----------|
| Old         | Copper-nickel | Copper-nickel | Copper-nickel |
| New         | Nickel Brass Clad Copper | Nickel Brass | Stainless Steel |

3.2 New (third) Series Coins
Looking at the new coins, we assume that the 50 and 20 cents cannot be discriminated, this is because they are made of the almost same material. So, they have the same elemental composition. Likewise, both 50 and 20 cents can be discriminated from the 10 cents, which is made of stainless steel. Generally, all the new coins can be discriminated from the old coins.

Similar separation in the PC scores is observed in Figures 7 and 9 which respectively refer to 20 cents and 50 cents old and new. Whereas, the scatter plot Figures 10 and 11 of old coins of 10, 20 and 50 cents show two clusters.

The cluster of 10 cents is well-separated from the mixed-up cluster of scores of 20 and 50 cents. Clearly, 20 and 50 cents are not discriminable using PCA. Similarly, in Figures 12 and 13, no clear separation between the scores of new coins of 10, 20 and 50 cents are observed making them indistinguishable by PCA. Supervised machine learning techniques may prove helpful in the discrimination of indistinguishable part of this work, which will be the extension of this work.

3.3 LIBS Spectra and PCA
Because of the bulk spectral data we obtained, it was difficult for us to analyze them. Therefore, we employed PCA to help us reduce and compress the data by choosing only principal components (PCs). Even from the LIBS spectra, it will be difficult to analyze the spectral lines.

Figure 3. New series of Malaysian coins

Figure 4 illustrates the spectral lines for the 10 cents old and coins, whereas Figure 5 shows the PCA scores and analyses for the same 10 cents old and new. PCA discriminates very clearly between old and new coins, however could not clearly discriminate between the new coins of 20 and 50 cents. And could not discriminate any from the set of old coins. The reason being the use identical materials for making these coins. The difference in LIBS spectra of two samples arises only if there exists difference between the compositions of the two.

Figure 5, is the scatter plot between PC scores of new and old coins of 10 cents. A clear separation is obtained because of the difference in the materials used to make these coins. Coin of old 10 cents is
made of copper-nickel while the coin of new 10 cents is made up of stainless steel. This is the difference in the material that causes a variance in LIBS data and not the shape of the material.

Figure 4. (a) 10 cents old and (b) 10 cents new spectral lines.

Figure 5. Scatter plot between PC scores of new and old coins of 10 cents.
Figure 6. (a) 20 cents old and (b) 20 cents new spectral lines.

Figure 7. Scatter plot between PC scores of new and old coins of 20 cents.
Figure 8. (a) 50 cents old and (b) 50 cents new spectral lines.

Figure 9. Scatter plot between PC scores of new and old coins of 50 cents.
Figure 10. old 50, 20 and 10 cents spectral lines.

Figure 11. Scatter plot between PC scores of old coins of 50, 20 and 10 cents.

Figure 12. new 50, 20 and 10 cents spectral lines.
4. Conclusion
It is clear, the LIBS technique has the capability to perform discrimination and differentiation of a variety of samples no matter how minute the differences in the elemental composition may be. There was a clear difference between the new coins and the old ones according to the PCA based on LIBS spectra. There was little difference or discrimination for the old coins - this is because they are made of almost same material. For the new 50 and 20 cents, there was no discrimination – this is because the same compositional material was used. LIBS technique was able thus to perform the effective discrimination and classification of coins, as such, it is an effective technique for classification and discrimination of a variety of samples with even minor differences.

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References
[1] De Giacomo A, et. al. 2014 Plasma processes and emission spectra in laser induced plasmas: a point of view. Spectrochimica Acta Part B: Atomic Spectroscopy 100 180-188
[2] Bhatti K, et. al. 2010 Electrons emission from laser induced metallic plasmas. Vacuum 84(7) 980-985
[3] Haider Z, et. al. 2016 Plasma diagnostics and determination of lead in soil and phaleria macrocarpa leaves by ungated laser induced breakdown spectroscopy. Analytical Letters 49(6) 808-817
[4] Runge E, Minck R and Bryan F 1964 Spectrochemical analysis using a pulsed laser source. Spectrochimica Acta, 20(4) 733-736
[5] Radziemski L J et. al. 1983 Time-resolved laser-induced breakdown spectrometry of aerosols. Analytical chemistry 55(8) 1246-1252
[6] Radziemski L and Cremers D 2013 A brief history of laser-induced breakdown spectroscopy: from the concept of atoms to LIBS 2012. Spectrochimica Acta Part B: Atomic Spectroscopy 87 3-10
[7] Rakovsky J, et. al. 2014 A review of the development of portable laser induced breakdown spectroscopy and its applications. Spectrochimica Acta Part B: Atomic Spectroscopy 101 269-287
[8] Baudelet M and Smith B W 2013 The first years of laser-induced breakdown spectroscopy. *Journal of Analytical Atomic Spectrometry* **28**(5) 624-629

[9] Arab M, et. al. 2015 Characterization of pollution indices in soil surrounding a power plant by laser induced breakdown spectroscopy. *Analytical Letters* **48**(2) 360-370

[10] Chaudhary K, et. al. 2015 Laser-Induced Graphite Plasma Kinetic Spectroscopy under Different Ambient Pressures. *Chinese Physics Letters* **32**(4) 043201

[11] Villas-Boas P R, et. al. 2016 Laser-induced breakdown spectroscopy to determine soil texture: A fast analytical technique. *Geoderma* **263** 195-202

[12] Sankaran S, Ehsani R and Morganc K T 2015 Detection of Anomalies in Citrus Leaves Using Laser-Induced Breakdown Spectroscopy (LIBS). *Applied Spectroscopy* **69**(8) 913-919

[13] Guang Y, et. al. 2015 Rock and soil classification using PLS-DA and SVM combined with a laser-induced breakdown spectroscopy Library. *Plasma Science and Technology* **17**(8) 656

[14] Castro J P and Pereira-Filho E R 2016 Twelve different types of data normalization for the proposition of classification, univariate and multivariate regression models for the direct analyses of alloys by laser-induced breakdown spectroscopy (LIBS). *Journal of Analytical Atomic Spectrometry* **31**(10) 2005-2014

[15] Costa V C, et. al. 2017 Identification and classification of polymer e-waste using laser-induced breakdown spectroscopy (LIBS) and chemometric tools. *Polymer Testing* **59** 390-395

[16] Arab M, et. al. 2014 Comparison study of two commercial spectrometers for heavy metal analysis of laser induced breakdown spectroscopy (LIBS). *Photonic Sensors* **4**(1) 63-69

[17] Zhang T, et. al. 2016 Classification of steel samples by laser-induced breakdown spectroscopy and random forest. *Chemometrics and Intelligent Laboratory Systems* **157** 196-201

[18] Campanella B, et. al. 2017 Classification of wrought aluminum alloys by Artificial Neural Networks evaluation of Laser Induced Breakdown Spectroscopy spectra from aluminum scrap samples. *Spectrochimica Acta Part B: Atomic Spectroscopy* **134** 52-57

[19] Pokrajac D, et. al. 2010 Performance of multilayer perceptrons for classification of LIBS protein spectra. In *Neural Network Applications in Electrical Engineering (NEUREL), 2010 10th Symposium* 171-174

[20] Xia H and Bakker M 2014 Reliable classification of moving waste materials with LIBS in concrete recycling. *Talanta* **120** 239-247

[21] Chaudhary K, Rizvi S Z H and Ali J 2016 Laser-Induced Plasma and its Applications. In *Plasma Science and Technology—Progress in Physical States and Chemical Reactions*. InTech

[22] Unnikrishnan V, et. al. 2013 Analytical predictive capabilities of laser induced breakdown spectroscopy (LIBS) with principal component analysis (PCA) for plastic classification. *RSC Advances* **3**(48) 25872-25880

[23] Vítková G, et. al. 2014 Comparative study on fast classification of brick samples by combination of principal component analysis and linear discriminant analysis using standoff and table-top laser-induced breakdown spectroscopy. *Spectrochimica Acta Part B: Atomic Spectroscopy* **101** 191-199

[24] Italiano A, et. al. 2013 A comparative analysis of old and recent Ag coins by XRF methodology. In *3rd Workshop-Plasmi, Sorgenti, Biofisica ed Applicazioni*

[25] Torrisi L, et. al. 2013 Silver coins analyses by X-ray fluorescence methods. *Journal of X-ray science and technology* **21**(3) 381-390

[26] Linke R, et. al. 2003 Determination of the provenance of medieval silver coins: potential and limitations of X-ray analysis using photons, electrons or protons. *X-Ray Spectrometry* **32**(5) 373-380

[27] Torrisi L, et. al. 2009 Laser and electron beams physical analyses applied to the comparison between two silver tetradrachm greek coins. *The European Physical Journal D-Atomic, Molecular, Optical and Plasma Physics* **54**(2) 225-232