Laser Induced Breakdown Spectroscopic Investigation and Discrimination of Sabah’s Pearl

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Abstract. Natural pearls have different composition that give them specific properties such as colour, lustre effect and can be classified based on differentiation of various constituents such as crystal phase and the presence of various minerals. The aim of this study was to develop a fast, simple, and non-destructive method for discrimination of the popular Sabah’s pearl that commonly used for bracelet, earring, and necklace. In order to discriminate pearls of different colours, emission spectroscopic method, namely laser-induced breakdown spectroscopy (LIBS) complimented with principal component analysis (PCA) was used. PCA model showed that the first principal component explained 96.44% of the total variance. Calcium, Mercury, and Barium elements mainly deexcited at wavelength 600 to 900 nm attributing to the most effective variables for PC1 while Manganese, and Silicon content were useful in defining PC2. PCA demonstrated clear clustering of pearl samples of different colors. Thus, became a major indicator for successful discrimination of natural pearls of various colors using LIBS spectral data. We can confidently say that this can be made available to use by gems industry for performing a fast quality control of inflowing raw organogenic gems.

1. Introduction

Organic matrix composites (OMC) is potentially being developed with high specific stiffness suitable for space [1], electroluminescent [2], antennas [3], and high temperature [4] applications. OMC are candidate for replacement of alloy which offer thermal stability and durability. At present, micro- and nanohybrid materials are considered to provide an optimal balance of strength, durability, esthetics and handling. Nanohybrid materials, which combine OMC and nanoparticles demonstrated to gain good mechanical strength.

Pearl is one of organogenic gems, natural form of polymorphs calcium carbonate, (CaCO₃) used for centuries. The dome shape and it’s shining properties make pearl as a symbol of attractiveness to its user therefore create demand for pearl production. In the last decades, increase of demand of this gems and advance of communication technology plead to human intervention to supply pearl across the globe. Pearls are originated from CaCO₃ concretions, caused by biomineralization of both freshwater and saltwater mollusks [5]. Natural pearl is formed accidentally within a mollusc. Pearl is produced in three main ways; natural, cultivation, and synthetic. Pearl is naturally formed in marine oysters (Pinctada and Pteria). Cultured pearls are formed by transplantation (with implantation of bead) which layered molluscs within pearl sac. Cultured pearls are the result of a grafting process being cultivated and...
harvested from a certain shell species (e.g. Pinctada maxima, Pinctada margaritifera, Pictada fucata, Unio) [6]. Pearls are classified by external appearance (colour, shape, et.al). The increase of acidification in the sea had threaten marine species where it reduced calcification rates and dissolution of calcareous structures of marine species [7], especially pearls.

Under microscope, nacreos (natural and cultivated pearl) formed layer pattern of stacked aragonite and vaterite. Laser induced breakdown spectroscopy (LIBS) combined with multivariate analysis tools which is principal component analysis (PCA) was used to discriminate different type of pearls sample. This work focusing on mapping, identifying, and tracing elements that currently exist on the pearl’s surface produced naturally from Sabah, Malaysia. A better understanding of the underlying construction principles of naturally occur organic composite might help designing better composite materials and potentially be applied in the field such as macromolecules host and drug delivery systems.

2. Experiment

High energy laser pulse from Nd:YAG, Litron Lasers emitted 1064 nm was operated in ambient environment and room temperature. A mirror deflects laser beam from horizontal to vertical axis. A biconvex lens then focuses the laser beam onto the sample surface. The high energy laser pulse with 600 mJ and 5 ns pulse duration hits the sample target, in this case pearl sample, and instantaneously forms plasma plume. A spectrometer, Ocean Optics USB2000+, with wavelength range, 600-900 nm, and resolution 0.5 nm collect the light emission from plasma with integration time 10 ms. Efficient detection is needed when rapid analysis is important and only a small fraction of the surface is being processed. Therefore, light emission result from de-excitation from lased induced breakdown phenomena certainly captured by spectrometer via fiber optics cable. The LIBS experiments were performed with combination of principal component analysis (PCA). The pearl samples used in this study are shown in Figure 1. The sample numbers are ordered from brightest to darkest color. Figure 2 shows the experimental setup for the LIBS system. All measurements were carried out by 15 shots per sample. The average of these measurements was used as the dataset in data analysis. Spectral lines of interest were identified using NIST [8] Atomic Spectra database and literature.

![Figure 1. Seven different colours of Sabah’s pearl used for this study, according to colour code, from left: (1) white, (2) cream, (3) yellow, (4) copper, (5) pinkish, (6) dark green, and (7) black.](image1)

![Figure 2. LIBS experimental setup to collect spectrum of aragonite-vaterite on pearl’s nacre.](image2)
3. Result and Discussion
In this research, laser induced breakdown on pearl’s surface, mainly build up by aragonite and vaterite, had been carried out. The spectra of light emission spectrum by different pearl sample have been recorded with minimal pre-treatment. The analysis method has been implemented by predicted chemical parameters from spectrum. The emission spectra of pearl samples in this study shown in Figure 3.

3.1. Optical Emission Spectroscopy

![Figure 3. LIBS spectra of 7 identified colours of Sabah’s pearl obtained by optical emission spectroscopy with elemental mapping from NIST database.](image)

Table 2. Atomic transition line and intensity for different colour of pearl obtained by LIBS spectra.

| Wavelength (nm) | Element | Transition | Intensity | White Cream | Yellow | Copper | Pinkish | Dark Green | Black |
|-----------------|---------|------------|-----------|-------------|--------|--------|---------|------------|-------|
| 617.160         | Sn I    | 5s²5p7p ³P°₀→5s²5p6s ³P₁ | 1972436827 23512 41189 32178 52796 52402 |
| 644.350**       | Mn I    | 3d⁵(⁵D)⁴P ³D₂/₂→3d³4s² | 8326 14165 9281 18715 15982 24888 21730 |
| 646.743         | Mn II   | 3d³(⁶S)⁴d ⁵D₂→3d³(⁴G)⁴P ³F°₃ | 6788 12976 8251 16874 14001 23808 20867 |
| 672.185         | Si I    | 3s³3p6d ¹D₂→3s³3p4⁴P₁ | 3996 6065 3694 8074 7641 10581 8666 |
| 714.815         | Ca I    | n/a | 5602 5566 3687 10677 11073 11278 8796 |
| 787.780         | Ba I    | 6s6d ¹D₂→6s6p ¹P₀ | 1524533400 16283 41457 34488 57035 55126 |
3.2. Principle Component Analysis of LIBS Spectra

Spectra obtained from seven pearls samples have large and complex data. Therefore, spectral data obtained by LIBS were used in combination PCA for classification of different colored pearls colour. PCA is a linear dimensionality reduction technique that is used to extract information from large dimensional data set and reduced to small dimensional data set. The main goal is to reduce the complexity of a problem by projecting the feature space to a lower-dimensional space so that less correlated variables are considered in a machine learning system. The PCA technique has been chosen to classify and discriminate data sets mainly because it removes correlated features. This feature is not easy to be visualized for datasets with many features. So, in order to reduce the number of features in the dataset, PCA plays a very useful role.

The evaluation of loadings plot allows to find the variables contributing to each principal component (PC). Positive loading indicates that variable and PC are positively correlated. Figure 4 shows the loading plot of the PC for pearls sample in this study.

![Loading plot](image-url)

Figure 4. Loading plots for principle component of the Sabah’s pearl.
The result of the principal component analysis shows that about 96% of total variation is explained by the first principal component, while nearly 2% by the second principal component. According to the NIST database mapping and PCA analysis, the PC1 is characterized by Barium, Mercury and Calcium elements while the PC2 is characterized by Manganese and Silicon elements. Thus, indicates the elements contribute mainly toward existence of different colour of Sabah’s pearl.

By using scree plot, we can decide the number of principal components to be used. Figure 5 shows the scree plot of PCA analysis for pearl spectra. [Need further explanation about Figure 5]

![Figure 5. Scree plot for principle component analysis of pearls’ spectra.](image)

The score plot data shows the projection of each observed sample to the principal components. Figure 6 shows the score plot of pearl’s classification referring to pearls’ colour.

![Figure 6. Scores plot for principle component analysis of (7) seven identified colour of Sabah’s pearl.](image)
The score plot in Figure 6 shows the location of pearl in the multivariate space of three principal component score vectors. The scores are clearly clustered in seven groups. The darkest group from ‘Black’ pearl placed at the least of PC1 and PC3 scores but high in PC2 score showing negatively correlated with Barium, Mercury and Calcium. Meanwhile, the ‘Copper’, ‘Pinkish’, and ‘Dark Green’ pearl have least variance in PC3 scores but high in PC2 scores. This correlate that those three pearls are having positive correlation with Manganese and Silicon. Furthermore, the brightest group from ‘White’ pearl exhibit highest score in PC3 and PC2.

Based on the overall results concerning different spectra analysis, PCA proved to be a useful method to identify the most effective variables and to point out quickly the relationship among the variables. In addition, PCA allows rapid differentiation, classification, and identification of LIBS spectrum features, which variable are correlated to each other. The arrangement of spectrum features in relation to the variables, substantially differentiate presence of elements, thus discriminate group of pearl, indicating different pearl’s colour characteristics. Moreover, the existence of considerable distance within groups remarkably shown in scores plot.

4.0 Conclusion
Calcium carbon polymorphs that is naturally grown on pearl’s nacre appear to present broad range of mineral and elements characteristics. Different element composition of the nacre layer on the surface of the pearl have been successfully discriminated and classified using principal component analysis technique. The features of excitation wavelength from 600 to 900 nm variables contributing to 96% of the total variance. The spectroscopic analysis reveals dark colour of pearl contains high Manganese and Silicon while bright colour of pearl mainly contains Barium, Mercury, and Calcium elements.

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