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Elemental Tracing of Original with Plastic Pearl by Atomic Emission Spectra

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Abstract: Pearls continued to be used luxuriously, and their lavish use is best reflected in the famous mosaic picture. The production of imitating pearl makes user muddled by too much same-looking items. Fast and reliable technique is demanded to distinguish between imitate and original ones. The objective of this study is being able to differentiate between natural pearl and plastic pearl using laser ablation technique. High energy Nd:YAG laser pulse was focused on those samples and evaporise samples in form of plasma plume. Upon deexcitation of the excited electron, electromagnetic radiation which was not being absorbed by the plasma itself was emitted throughout the space and create small crater on samples. The light emission from the plasma was collected through spectrometer and analyzed carefully. The elemental mapping was being carried by matching the central peak of emission lines with standard one. Plotting of optical emission spectrum recorded easily distinguish between original and imitate ones. Moreover, elemental tracing showing existence of few elements which is not available in the plastic pearl includings Fe, Sn, Mn, Si, Hg, Mg, and Ba. The study implies optical emission spectroscopy as fast technique to differentiate original and imitate organogenic gems. In future, quantification technique could be applied to identify quantity of dissolving elements in this fascinating gems

Keywords: Pearls, Calcium Carbonate Polumorphs, Laser, Atomic Lines

1. Introduction

Pearl is one of organogenic gems used for centruies. The dome shape and it's shining properties make pearl as a symbol of attractiveness to it's user therefore create demand for pearl production. In the last decades, increase of demand of this gems and advance of communication technology plead to

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human intervention to suppy pearl across the globe. Pearls are originated from calcium carbonate ($CaCO_3$) concretions, caused by biomineralization of both freshwater and saltwater mollusks [1]. Natural pearls is formed accidentally within a mollusc. Pearl is produced in three main ways;by natural, by cultivation, and synthetic way. 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) [2]. Imitate pearls, or synthetic ones, are made from plastic, polymer or tridacna gigas shells [3]. Pearls are classified by external appearance (colour, shape, et.al). As there is commonly a large price gap between natural pearls and imitate pearls, the trade relies on specialized laboratory analysis to distinguish original and imitate pearls. The analysis are based on radiography, X-ray luminescence, and X-ray computed μ-tomography, combined with X-ray fluorescence (EDXRF), Raman microspectrometry, UV-Vis-NIR reflectometry and meticulous microscopic examinations [4]. The increase of acidification in the sea had threaten marine species where it reduced calcification rates and dissolution of calcareous structures of marine species [5], especially pearls.

Under microscope, nacreos (natural and cultivated pearl) formed layer pattern of stacked aragnonite which is not present in the synthetic form. In order to determine authentic pearl, analysing method by observing under microscope only is not sufficient since it does not represent existing elements and sometimes time consuming and costy. Therefore, we have selected laser ablation as one of the fast technique to identify presence of elements in pearls sample. This work focusing on mapping, identifying, and tracing elements thus significantly differentiate between original and imitate pearls.

2. Materials and Methods

An original pearl obtained from Sabah, Malaysia was used in this study. The pearl is bright pink in colour and has shiny look with a dome shape with some irregularities. The diffused light from the nacre layers causes the color of pearls. They can appear in many colors in the hue circle, such as yellow, orange, pink, purple, blue, green, and black, but usually in lower saturations. The colors of pearls are caused by color pigments inside the nacre layers, and by some trace element compounds. The color of a pearl is usually the same as the color of the nacreous lining of the mollusk. In contrast, the plastic pearl is also pink in colour with sphrerically symmetric shape collected from gift shop.

Laser ablation technique was chosen in this study to study the authenticity of pearl since it takes less time to capture signal and does not require sample preparation. The experimental setup deployed in this study shown in Figure 1 below. A high energy nanosecond Nd:YAG laser pulse (Litron Lasers Ltd) was used as laser source.

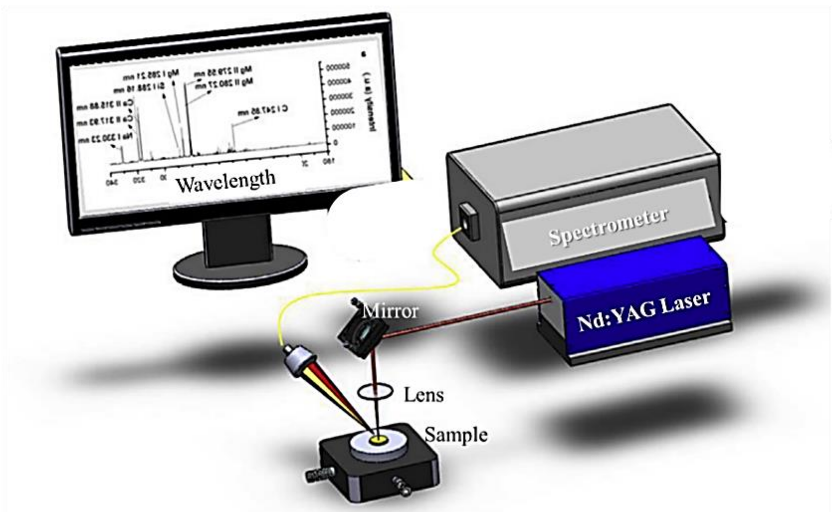

Figure 1: Experimental setup for laser ablation of pearl

The laser emit infrared radiation at wavelength 1064 nm with pulse width 6-10 ns, repetition rate 1 Hz, and energy maximum at 600 mJ. The laser beam was focused by biconvex lens with focal length 8 cm direct into pearl target. The plasma formation and light emission was collected by fiber optic which was connected with spectrometer model Oceanoptics USB 2000+. The integration time is 100 ms.

3. Results and Discussion

The results represents data of emission line and analysis of the pearl study. The emission line was mapped with database of National Institute of Standard and Technology (NIST). Pearls are composed of 82%–86% calcium carbonate (as aragonite $CaCO_3$) ,10%–14% conchiolin ($C_{32}H_{43}N_9O_{11}$), the organic binding agent, and 2%–4% water [6]. However, the main component of pearls, calcium carbonate ($CaCO_3$), is one of the most common earth minerals. Calcium carbonate most of time laid down in concentric layers around the nucleus.

3.1 Optical Emission Spectrum of Original and Plastic Pearl

The spectrum of pearl capture by spectrometer and elemental mapping within the NIST website carried shown in Figure 2.

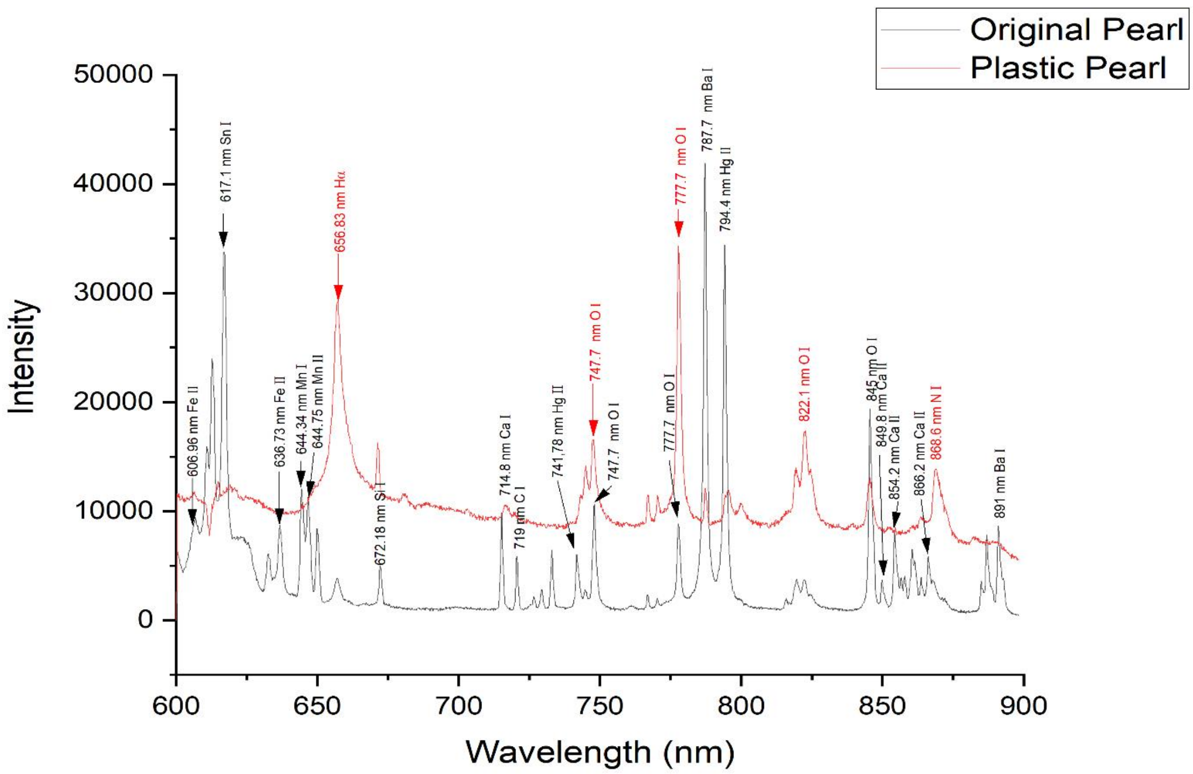

Figure 2: Emission spectrum obtained by laser ablation on original pearl and plastic one

The elemental mapping in Fig. 2 showing clear picture of distinguishable of emission spectrum as produced by original (black line) by original and imitate pearl (red line) as captured by spectrometer in the range of ultraviolet (UV) to visible (Vis), 600 nm to 900 nm. Table 1 shows the list of peak found in the spectrum and comparison with the standard atomic lines based on NIST database. According to

NIST database, the lines from 787.7 nm of Ba I line has higher transisiton probability than Mg II lines, therefore the elements is selected. Since pearl made of calcium carbonate, the calcium elements were available in most of the lines at 714 nm, 849 nm, 854 nm, and 866 nm.

Table 1: Spectroscopic data of the relevant emission spectral lines. taken from reference [7] **found in original Pearl.**

Wavelength emitted, λ	Wavelength Ref. λ_{ref}	Elements	Relative Intensitites	Transition Probability, A (1/s)	Initial Energy Level, E_i (cm^{-1})	Final Energy Level, E_f (cm^{-1})
606.96	606.96694	Fe II	40	$7.1x10^6$	86 416.370	102 887.172
617.10	617.15980	Sn I	58	$4.9x10^6$	34 914.282	51 113.059
636.73	636.7426	Fe II	60	$3.9x10^6$	88 157.176	103 857.804
644.34	644.350**	Mn I		$4.7x10^5$	30 425.71	45 940.93
646.75	646.743	Mn II			66 686.739	82 144.603
672.18	672.1853	Si I	100	$3.4x10^6$	47 284.061	62 156.816
741.78	741.7864	Hg II	18000	$1.2x10^7$	95 714.406	109 191.648
747.70	747.724	O I	100			
777.70	777.539	O I	750	$3.69x10^7$	73 768.200	86 625.757
787.16	787.738	Ba I	2	$1.6x10^6$	18 060.261	30 750.672
794.13	794.4555	Hg II	25000000	$4.3x10^7$	95 714.406	108 298.183
891.04	891.5013	Ba I	80		12 266.024	23 479.976

Note-** represent Ritz wavelength, the derived wavelength in vacuum UV region.

Oxygen triplet found at 845 nm is better suited than oxygen 777 nm line [8]. Apparently, both elements were present in both spectrum. Result of pearl spectrum showing existence of Barium, Ba, the alkaline earth metal in the linewhich is was determined earlier using X-ray luminescence [9]. This study also showing pearls rich in Magnesium as high intensity of emission line at 787 nm prominently appear. Silicon, Si element also found in original pearls appear at line 672 nm which indicate it originated from sea as it dissolve little amount of sand. Pearl also rich in Manganese, Mn which appear in the line 644.34 nm and 644.75 nm.These element are not available in the plastic pearls after elemental tracing practices.

3.2 Dissolving Elements

Mercury (Hg) has been reported dissolved in pearl in China [10]. The mercury element traced in this study indicated by atomic lines appear at 741 nm and 794 nm. Tin (Sn) elements might also become one of dissolved metals found in pearls. Study shows that there are possibilitites seafood may contains toxics element such as Hg and Sn [11, 12].

4. Conclusion

In conclusion, pearl aunthenticiy will be able to be determined by using fast technique, laser ablation. Original pearl contains multiple elements including Mn, Ba, and Si which does not exist in imitate pearl. Main difference is the the calcium elements which is abundance in original pearl came from calcium carbonate compound. Pearl also has potential to dissolve some toxic elements including Sn and Hg which are traced in this study appeared prominently at line 617 nm and 794 nm.

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