Identification of Dyed Golden South Sea Pearls using UV-Vis and PL Tests
利用紫外 - 可見光和拉曼光致發光光譜檢測染色黃金南洋珍珠

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Fig. 1 Typical natural-colour (top) and dyed (bottom) pearls used in this study

作者利用紫外—可見光光譜和拉曼光致發光光譜對112顆黃金色南洋珍珠進行顏色檢測，從而分辨天然和染色珍珠的分別，證實兩者皆能夠提供有效的證據，對寶石檢測有莫大的效益。

Introduction

Deep yellow or "golden" seawater cultured pearls are formed within Pinctada Maxima oysters that live in the South Pacific. Pearls of a naturally deep and uniform gold colour are rare because the colour of pearls is greatly influenced by many factors such as the mother oyster and the epithelium of the graft tissue as well as marine environmental factors such as the temperature, depth, and chemical composition of the seawater. Ever since the appearance, in the late 1990s, of deep gold coloured pearls, which were actually dyed white or light yellow South Sea pearls, the distinction between natural-colour and dyed golden pearls has been an important issue. Earlier dyed golden pearls could be identified with routine gemmological tests including the detection of dye traces on the surface or within drill holes... in some cases, along with long-wave UV fluorescence tests. However, as identification became much more difficult due to the continual improvement of treatment techniques, spectroscopic analysis including UV-Vis became a necessity.

A total of 112 South Sea golden pearl samples with no drill holes, 51 natural-colour and 61 dyed, were studied using gemmological and spectroscopic tests. Even though some of the samples displayed artificial colours, which suggested dye treatment, most of the natural-colour and dyed pearls were indistinguishable in their colour. Dye traces were not observed on the surface under magnification, and a considerable number of dyed pearls showed fluorescence similar to that of natural-colour pearls under long-wave UV light. In short, it had become clear that traditional gemmological testing was of limited use in the identification of dyed golden pearls.

UV-Vis Analysis

The 112 golden pearl samples ranging from 9 mm to 15 mm were further analysed using a Jasco V-600 UV-Vis spectrophotometer. The representative UV-Vis spectra of 51 natural-colour golden pearls with a variety of colour variations are shown in Fig. 2. The natural-colour samples tend to have stronger conchiolin-related absorption at 280 nm than the dyed samples, and show a broad absorption band between 310 nm and 500 nm with local reflectance troughs at about 360 and 430 nm. Most of the natural-colour samples exhibit stronger absorption at

360 nm than the absorption at 430 nm. Only about 10% (5 samples) of the natural-colour samples show similar levels of absorption at 360 nm and 430 nm.

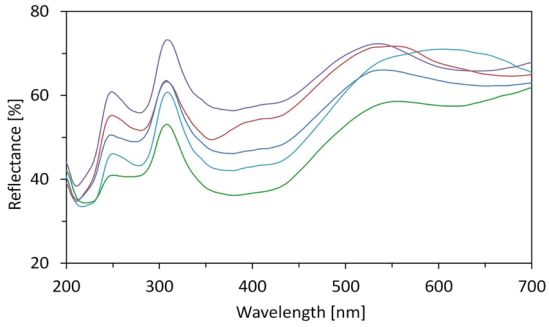

Fig. 2 UV-Vis spectra of natural-colour golden pearls

61 dyed golden pearls could be classified into several groups according to the UV-Vis spectral patterns. The first group has a broad absorption band centred at around 450 nm (Fig. 3), without the 360 nm reflectance feature observed in natural-colour golden South Sea pearls. This was the most commonly observed pattern in the dyed golden pearl samples (42 samples, or 69%), and the dyed pearls in this group are easily distinguishable from natural-colour pearls owing to the obvious differences in their UV-Vis patterns.

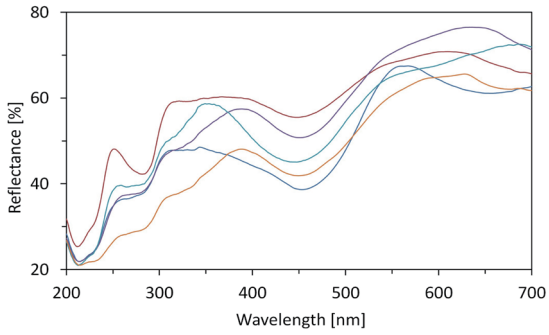

Fig. 3 UV-Vis spectra of dyed golden pearls (Group 1)

The second group (16 samples, or 26%), a type often seen in recent years, displays the most similar pattern to that of natural-colour pearls. As shown in Fig. 4, the pearls in this group have a broad absorption band between 310 nm and 500 nm, as also seen in the spectra of natural-colour pearls, but with local reflectance troughs at shifted positions, at about 385 nm and 440 nm. As a result of this trough position shift, the 310~500 nm band looks narrower than that of natural-colour pearls. Also, the absorption at 440 nm is stronger than the absorption at 385 nm; another feature different from most natural-colour golden pearls.

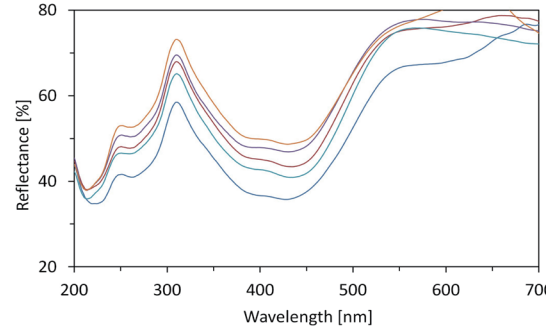

Fig. 4 UV-Vis spectra of dyed golden pearls (Group 2)

The absorption pattern of the third group (2 samples or 3%) also displays a broad band between 310 nm and 500 nm, with prominent absorption peaks at 330 nm and 440 nm as shown in Fig. 5. Dyed golden pearls in this group are easily distinguishable from the natural colour pearls owing to their different absorption peak positions.

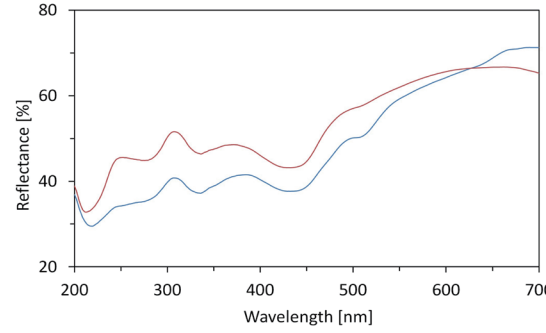

Fig. 5 UV-Vis spectra of dyed golden pearls (Group 3)

One sample, however, did not fit into any of the three groups. Fig. 6 compares the UV-Vis spectrum of this a-typical dyed golden pearl (solid red line) with that of a natural-colour golden pearl (dotted green line). The dyed sample also displays an absorption band between 310 nm and 500 nm, with reflectance troughs at 350 nm and 420 nm, shifted toward lower wavelength compared to natural-colour pearls. Another notable feature is that the absorption at 420 nm is stronger than the absorption at 350 nm, similar to the dyed pearls in the second group and the opposite of the pattern seen in most natural-colour pearls.

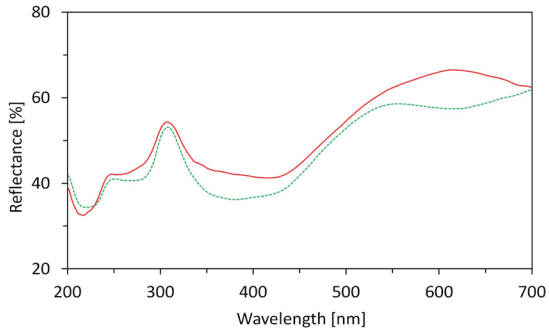

Fig. 6 UV-Vis spectrum of an a-typical dyed golden pearl (solid red line) compared to that of a natural-colour (dotted green line) golden pearl

Photoluminescence (PL) Analysis

In a study on the identification of dye treatment in yellow and golden cultured pearls, C. Zhou et al. suggested that fluorescence analysis using PL spectroscopy could be useful for identifying some dyed pearls [3]. Later, M. Midori and H. Komatsu also analysed the fluorescence of pearls using Raman spectroscopy in their study of methods of identifying dyed golden pearls [4].

To test the usefulness of PL spectroscopy in the identification of dyed golden pearls, we performed PL measurements with 514 nm green laser excitation (Fig. 7). Selected samples from each group of natural-colour (18 samples) and dyed (16 samples) pearls were tested using an in-house Raman/PL spectrophotometer. The position of the sample was adjusted so that the main aragonite peak intensity at 545 nm was maximized under the 514 nm laser excitation prior to each of the PL measurements.

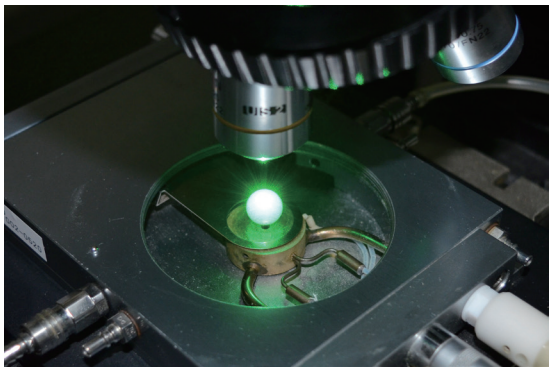

Fig. 7 PL measurement of a pearl with 514 nm green laser excitation

As shown in Fig. 8, prominent aragonite peak intensities are observed at 545 nm in the PL spectra of the naturally coloured samples, while much lower aragonite peak intensities are observed for the dyed samples. Our PL measurements also confirmed that the dyed pearl samples fluoresced at much higher levels than most of the naturally coloured pearl samples. However, fluorescence intensities were at the same level for a small number of both the natural-colour and dyed pearl samples. This suggests that the comparison of the ratio between the overall fluorescence intensity (F in Fig. 9) and the height of the main aragonite peak at 545 nm (A in Fig. 9), not the overall fluorescence intensity itself, could serve as a useful tool in identifying dye treatment. It is also interesting to note that the dye caused the fluorescence peak of the dyed pearls to shift to a higher wavelength than that of the natural-colour pearls.

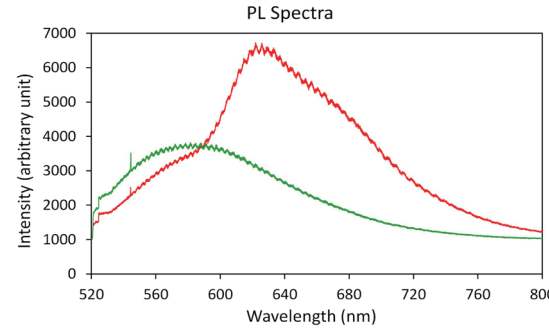

Fig. 8 PL spectra of natural-colour (green) and dyed-colour (red) South Sea golden pearls

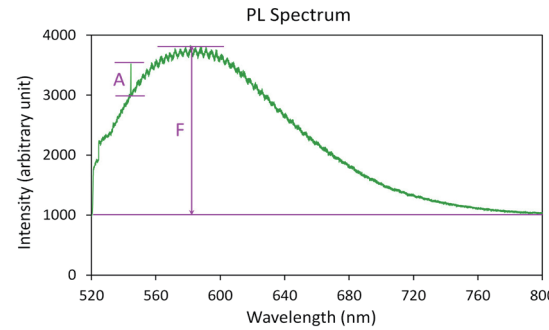

Fig. 9 Intensities of the aragonite main peak (A) and the overall fluorescence (F) are depicted in the PL spectrum of a pearl

The PL measurement results of 34 golden pearls (18 natural-color and 16 dyed) are summarised in Fig. 10, in terms of overall fluorescence intensity versus the F/A ratio. They are displayed in the logarithmic scale to cover the wide range of variance. The fluorescence intensities of dyed samples varied substantially due to the different dye materials used.

As presented in Fig. 10, while most of the natural-colour pearl samples fluoresce at lower intensities, fluorescence intensities of a few natural-colour samples overlap with those of dyed samples. Even though some of the natural-colour and dyed samples showed similar levels of fluorescence intensity (F), their aragonite peak intensities (A) being very different, natural-colour and dyed pearls could be separated by the F/A ratio. As shown in Fig. 10, the natural-colour pearl samples have lower F/A ratio (below 10 in this study) than the dyed-colour samples (16~270 in this study). Thus, comparing the F/A ratio helps separate naturally coloured from dyed golden pearls.

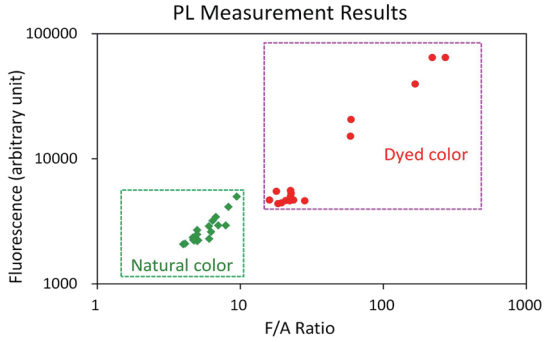

Fig. 10 The ratio between the total fluorescence and aragonite peak intensities (F/A) helps separate naturally coloured from dyed pearls

Conclusion

In conclusion, this study has demonstrated that dyed golden pearls can be identified by advanced techniques such as UV-Vis reflectance and PL spectroscopy. The results suggest that dyed golden pearls could be classified into several groups based on the UV-Vis absorption patterns, and distinguished from natural-colour golden pearls by comparing the absorption peak positions in the 310 nm~500 nm range. The peak positions of dyed pearls are either shifted from those of natural-colour pearls, or not present at around 350 nm.

We have also tested the usefulness of PL spectroscopy in identifying dye treatment of golden South Sea pearls. The ratio between overall fluorescence intensity and the height of the main aragonite peak under 514 nm laser excitation (F/A ratio) could also be helpful in separating natural-colour from dyed golden South Sea pearls.

References

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4. M. Midori and H. Komatsu (2014), A new method for identifying golden-lipped pearls (in Japanese), Margarite, No. 272, pp. 22-24.