UPDATE ON THE IDENTIFICATION OF DYE TREATMENT IN YELLOW OR "GOLDEN" CULTURED PEARLS

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Dye treatments in yellow or "golden" cultured pearls have improved to the point that some samples show little surface evidence. In addition to routine gemological observations, analytical techniques such as UV-Vis reflectance and Raman photoluminescence (PL) spectroscopy are critical to identifying the treatment. This study demonstrated three indications of dye treatment: broad reflectance features between 410 and 450 nm, the lack of a reflectance feature at 350 nm in the UV-Vis spectra, and intense fluorescence in the visible spectrum under 514 nm wavelength laser excitation. These diagnostic features may be used independently, even when no visual evidence of a dye exists.

Most dyed yellow or "golden" cultured pearls can be identified with routine microscopic observations. Dye residues usually accumulate within drill holes and surface blemishes, making them easy to detect with magnification. In some cases, long-wave UV fluorescence and UV-Vis reflectance spectrophotometry have been used to provide further evidence of dyeing (Elen, 2002; Qi et al., 2008; Chen et al., 2009). In recent years, though, GIA has begun receiving more "golden" cultured pearls with atypical UV fluorescence or UV-Vis reflectance characteristics but no evidence of dye residue. As processing techniques continue to improve, the authors believe it is important to update the trade on the situation to make sure that current identification methods are up to par with the treatments.

See end of article for About the Authors and Acknowledgments.
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The term "golden" is used to describe mid- to light-tone cultured pearls with a strong saturation in the yellow and orangy yellow hues (Gemological Institute of America, 2000). These cultured pearls are formed within *Pinctada maxima* (gold-lipped) oysters and have gained popularity over the years with the help of extensive marketing efforts by the industry (Shor, 2007; "The fabulous golden pearls of the Philippines...," 2010). In the meantime, increasing amounts of dyed "golden" South Sea and freshwater cultured pearls ("Supplier warns trade against dyed golden," 1998; Roskin, 2005) and, to a lesser extent, heat-treated "golden" products have also appeared on the market (Elen, 2001 and 2002). Detecting the treatment remains an important consideration in pearl identification, and an ongoing research investigation at GIA aims to provide solutions to the issue.

The present study focuses on the identification of eight sample groups of yellow or "golden" cultured pearl using routine gemological testing methods and advanced analytical techniques (figure 1). The known

Figure 1. These cultured pearls represent each of the eight sample groups. Top row: NSSP, NSSM, DSS, and DSS2. Bottom row: DSS3, DAK, DAK2, and DFW. Photo by Sood Oil (Judy) Chia.

TABLE 1. Cultured pearl sample groups and advanced testing techniques used in this study.

Group	Quantity	Geographic Source	UV-Vis	IR	Raman	PL
NSSP	10	Philippines	Tested all	Tested one	Tested one	Tested one
NSSM	8	Myanmar	Tested all	Tested one	Tested one	Tested one
DSS	7	Various[a]	Tested all	Tested one	Tested one	Tested one
DSS2	7	Various[b]	Tested all	Tested one	Tested one	Tested one
DSS3	7	Various[b]	Tested all	Tested one	Tested one	Tested one
DAK	10	Various[a]	Tested all	Tested one	Tested one	Tested one
DAK2	10	Various[b]	Tested all	Tested one	Tested one	Tested one
DFW	10	Various[a]	Tested all	Tested one	Tested one	Tested one
Heat-treated	3	Various[a]	Tested all	N/A	N/A	Tested all
Additional natural-color	>100	Philippines[c]	Tested all	N/A	N/A	Tested >50

[a]*Provided by Wuyi Wang*
[b]*Provided by Ahmadjan Abduriyim*
[c]*Provided by Jewelmer*

dyed samples exhibiting no traces of surface dye concentrations were singled out for analytical testing. The results suggest that advanced techniques such as UV-Vis reflectance and PL spectroscopy can detect the dye even when surface concentrations are absent. More than 100 naturally colored yellow cultured pearls were tested with the UV-Vis reflectance technique to provide additional reference datasets. Some of the latter were also tested with PL for the same purpose. Lastly, three heat-treated yellow cultured pearls were tested; their results are discussed briefly, since the sample size is minimal.

MATERIALS AND METHODS

A total of 69 yellow and "golden" cultured pearls ranging from 6.5 to 14 mm were studied. The eight sample groups consisted of:

- 10 naturally colored South Sea cultured pearls from the Philippines (NSSP)
- 8 naturally colored South Sea cultured pearls from Myanmar (NSSM)
- 21 dyed South Sea cultured pearls, in three separate groups (DSS, DSS2, and DSS3)
- 20 dyed akoya cultured pearls, in two separate groups (DAK and DAK2)
- 10 dyed freshwater nonbead-cultured pearls (DFW)

These samples were obtained from reliable sources who provided information on the samples' provenance. Real-time micro-radiography examination with a Faxitron CS-100-AC confirmed they were all cultured pearl products.

Each sample was examined with a standard gemological microscope, and photomicrographs were taken using a Nikon SMZ 1500 stereomicroscope. Fluorescence reactions were observed in a darkened room using a conventional 5-watt long-wave (366 nm) UV lamp. UV-Vis reflectance spectra were obtained using a PerkinElmer Lambda 950 UV-Vis spectrophotometer with an integrated sphere accessory. Selected samples from each group were also tested with a Thermo Nicolet Nexus 670 FTIR spectrometer and a Renishaw inVia Raman microscope.

The three heat-treated cultured pearls were obtained from a reliable source. In addition, more than 100 naturally colored yellow or "golden" South Sea cultured pearls (from Jewelmer) were tested using an Ocean Optics USB 2000+ UV-Vis spectrometer. This unit takes less than one minute to run a pearl sample, making it ideal for rapidly examining bulk quantities. Some of these cultured pearls were also tested with PL spectroscopy. A summary of the various sample groups and advanced testing techniques is provided in table 1.

RESULTS

Gemological Observations and UV Fluorescence. All 69 cultured pearls exhibited light yellow, orangy yellow, yellow, or strong yellow bodycolors of uniform color distribution except the dyed samples from

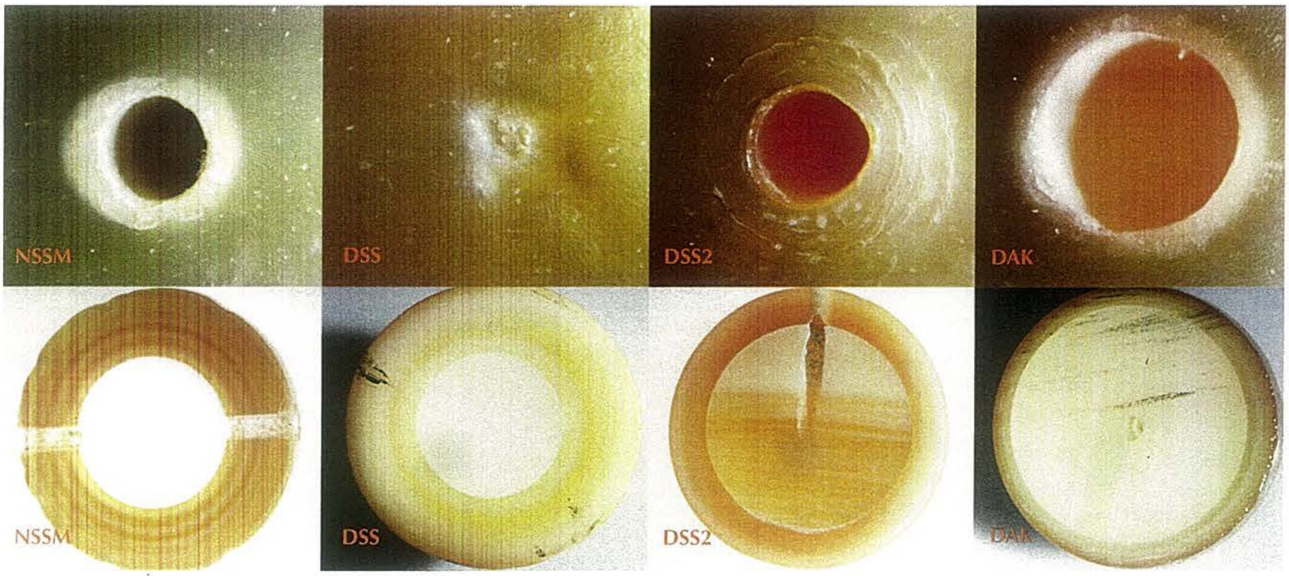


Figure 2. These microscopic images show the surfaces and cross-sections of representative samples from groups NSSM, DSS (high-quality dyed), DSS2 (low-quality dyed), and DAK (high-quality dyed). Photos by Chunhui Zhou; magnified 10×–70×.

group DSS3, which showed distinctly uneven color distribution. Under magnification, concentrated dye features were observed in three additional dyed groups (DSS2, DAK2, and DFW), while the other two dyed groups (DSS and DAK) showed no evidence of surface treatment (figure 2). To make matters even more challenging, cultured pearls from the DSS group did not possess drill holes, which serve to enhance the diffusion of the dye material, suggesting that a different dyeing technique was applied to them. Representative samples from groups NSSM, DSS, DSS2, and DAK were cut in half to observe the color distribution throughout their cross-sections. Typical concentric growth rings were noted on the nacre of the naturally colored sample, while the growth structures in the dyed cultured pearls were largely masked by the infiltration of dyes. The presence of a drill hole in the samples from DSS2 and DAK had caused the dye materials to diffuse into the bead used to culture the pearls.

In Brief

- The dyeing of yellow or "golden" cultured pearls from *Pinctada maxima* has been common for many years.
- While most dyed yellow or "golden" cultured pearls are readily identified by microscopic observation of dye concentrations, some have very clean surfaces lacking any evidence of treatment.
- These higher-quality dyed samples can be detected by broad reflectance troughs between 410 and 450 nm, a lack of a reflectance feature at 350 nm, or intense fluorescence in the visible spectrum under 514 nm wavelength laser excitation.

UV fluorescence generally followed the bodycolor of the sample. Naturally colored orangy yellow to strong yellow cultured pearls usually exhibited weak yellow fluorescence, while lighter yellow samples exhibited moderate to strong yellow fluorescence. It is a challenging task, however, to accurately and consistently describe fluorescence color, since there is no reference for comparison. In this study, dyed samples also showed varying degrees of yellow or orangy yellow fluorescence, but not distinctive enough to consistently separate them from the naturally colored variety. Samples from DSS3 and DFW showed uneven color distribution due to dye concentrations on their surfaces. General observations and measurements are shown in table 2.

UV-Vis Reflectance Spectra. Within each group, UV-Vis reflectance properties were generally consistent. Naturally colored samples (NSSP and NSSM) showed

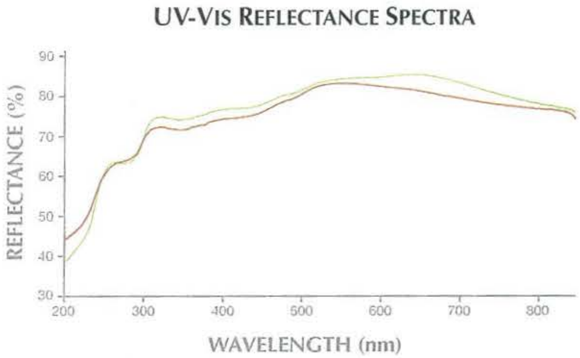


Figure 3. The UV-Vis reflectance spectra of representative samples from two naturally colored groups, NSSP (green) and NSSM (red), are compared.

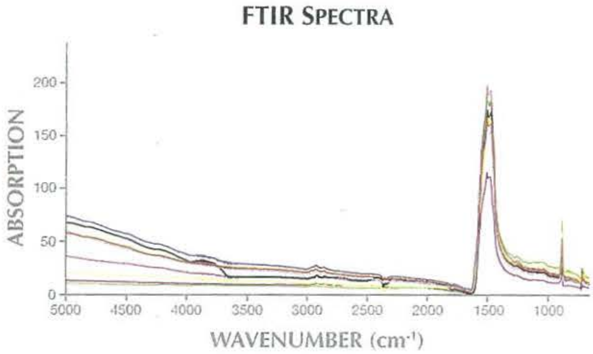


Figure 5. FTIR spectra of representative pearls from each of the eight groups are compared. All showed the same peaks related to the aragonite crystal structures of nacreous pearls.

decreasing reflectance toward the lower visible and long-wave UV range, with subtle local reflectance troughs at about 350 and 440 nm (figure 3). These reflectance troughs may be due to (but not equal to) absorptions at specific wavelengths. Cultured pearls from five of the dyed groups (DSS, DSS2, DSS3, DAK, and DAK2) all showed distinct reflectance characteristics within the same range, but with broader, more prominent, and sometimes shifted reflectance features between 410 and 450 nm, consistent with previous findings (Elen, 2002; Qi et al., 2008; Chen et al., 2009). Some of the dyed cultured pearls (DSS, DAK, and DAK2) also lacked the 350 nm reflectance feature, while others (DSS2 and DSS3) showed a steeper slope between 430 and 480 nm than that of naturally colored samples (figure 4), also consistent with previous findings. Dyed freshwater cultured pearls showed reflectance patterns similar to those of the naturally colored samples within the lower visible range, but lacked the 350 nm reflectance feature.

FTIR, Raman, and PL Spectroscopy Results. We performed infrared and Raman spectroscopy on representative samples from each of the eight groups. The FTIR spectra only showed the vibrational modes of aragonite, the major component of all pearls, dyed or naturally colored (figure 5). Raman spectroscopy was performed with both 514 and 830 nm lasers. The 830 nm laser gave much better peak resolution (figure 6),

Figure 4. These UV-Vis reflectance spectra are of representative cultured pearls from six dyed sample groups: DFW (black), DAK (violet), DAK2 (yellow), DSS (purple), DSS2 (greenish blue), and DSS3 (blue).

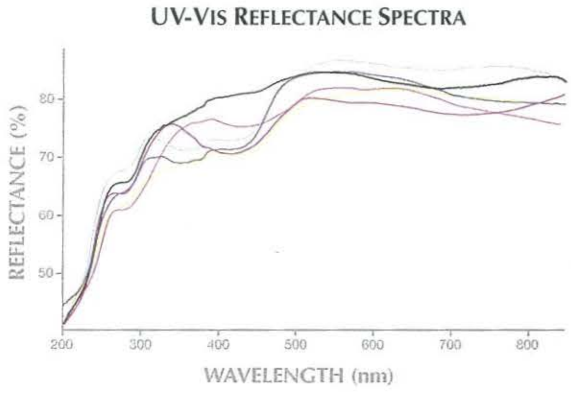


Figure 6. Raman spectra of representative samples from each of the eight groups are shown. All displayed the same peaks related to the aragonite crystal structures of nacreous pearls. The higher spectral intensity toward the lower wavenumber in some samples is due to their higher fluorescence.

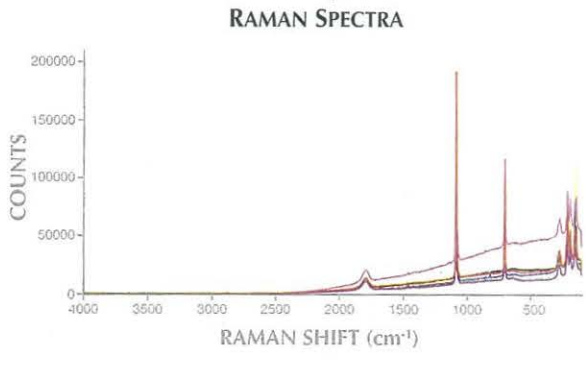


TABLE 2. General observations and measurements of the cultured pearls examined in this study.

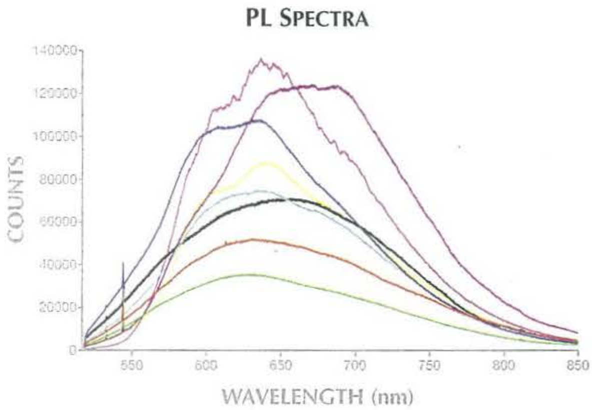
Type	Measurements (range)	Color	Drilling	UV fluorescence
NSSP	12–14 mm	oY/Y/Strong Y	N	Weak/Very Weak Y
NSSM	12 x 11 mm–10.5 mm	Light Y/Y/Strong Y	In some cases	Strong/Moderate/Weak Y
DSS	8–10 mm	oY/Y/Strong Y	N	Moderate/Weak/Weak Y
DSS2	10–13 mm	oY/Y	Y	Weak/Very Weak Y
DSS3	10–14 mm	oY/Y	Y	Moderate/Weak Y/Moderate oY (uneven)
DAK	7.85–8 mm	oY/Y	Y	Strong/Moderate Y
DAK2	6.5–7.5 mm	oY/Y	Y	Weak Y
DFW	9.5 x 8 mm–9 x 7.5 mm	Light Y/Y	Y	Strong Y/Weak oY (uneven)

Color abbreviations: Y (yellow), oY (orangy yellow).

while the 514 nm laser (data not shown) registered significantly higher background fluorescence in the dyed and naturally colored samples.

To clearly visualize the fluorescence characteristics of these samples upon laser excitation, we performed PL measurements. These confirmed that most of the dyed cultured pearls fluoresced at much higher levels than naturally colored pearls—in a few cases, reduced power had to be used to prevent peak oversaturation—making it a useful tool in identifying some cases of dye treatment (figure 7). A more useful way to look at the data, though, is to compare the ratio between overall fluorescence intensity (600–700 nm) and the height of the main aragonite peak at 545 nm (i.e., the F/A ratio; figure 8). Dominant or significant aragonite peak intensities were observed in the spectra of naturally colored samples, with the F/A ratio consistently below 5. For dyed samples, the ratio varied more due to the different dye materials used, but they were more likely to have F/A ratios of at least 10.

Figure 7. PL spectra of representative samples from each of the eight groups are shown: NSSP (green), NSSM (red), DFW (black), DAK (violet, 5% laser power), DAK2 (yellow, 50% laser power), DSS (purple), DSS2 (greenish blue), and DSS3 (blue). Naturally colored cultured pearls generally gave lower fluorescence upon laser excitation, while most dyed samples fluoresced at much higher intensity.



Additional Reference Collection Data Results. In addition to the 18 reportedly naturally colored yellow samples, we examined more than 100 reportedly naturally colored yellow to orangy yellow cultured pearls of various saturations using UV-Vis reflectance

Figure 8. In this representative PL spectrum, comparing the ratio between the total fluorescence (F) and intensity of the aragonite main peak (A) helps separate naturally colored from dyed cultured pearls.

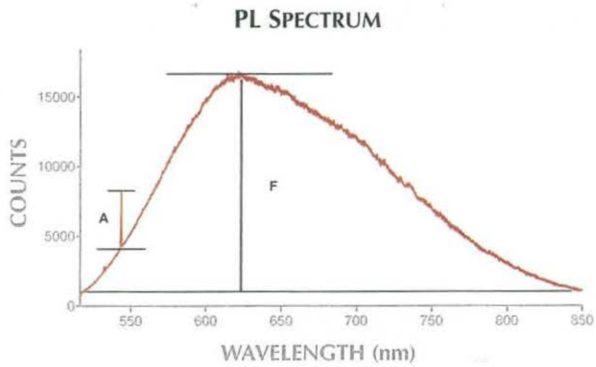


Figure 9. Naturally colored cultured pearls generally show consistent UV-Vis reflectance characteristics and less-intense PL features, which may be useful in identifying unknown samples. Photo by Adirote Sripradist.

and PL methods. These provided useful baselines for comparing unknown samples. The UV-Vis reflectance results of these naturally colored yellow samples showed consistent spectroscopic characteristics, similar to those observed in groups NSSP and NSSM (again, see figure 3). Low PL fluorescence signals (and F/A ratio) were also observed in all of the cultured pearls. Building and maintaining a spectral database from naturally colored yellow samples of various saturations (figure 9) is important for comparative analysis and identification of dye treatment.

Heat-Treated Yellow Cultured Pearls. In addition to dye treatment, heat-treated yellow cultured pearls have been reported (Elen, 2001). The exact mechanism of color alteration is still unclear. One theory suggests that heating changes the amino acid compositions of conchiolin proteins, altering their physical and chemical properties (Akiyama, 1978). Another possibility is that heating proteins and sugars (found in conchiolin) at high temperature under intermediate moisture levels and alkaline conditions will promote Maillard reaction, resulting in a color change similar to the browning effect caused by heating many kinds of food. The three reportedly heat-treated cultured pearls were tested using UV-Vis reflectance and PL spectroscopy. The UV-Vis spectra lacked the obvious broad reflectance pattern found in dyed samples, consistent with an earlier report (Elen, 2001) that their heat treatment did not involve any addition of dye materials. Yet the PL spectra showed extremely intense fluorescence, which could be useful in separating them from naturally colored samples. A brief summary of these results appears in box A.

DISCUSSION

The dyeing of cultured pearls has been a common practice for many years (Alexander, 1960; Liddicoat, 1962; Johnson and Koivula, 1999), and it can usually be detected through careful examination of the surface. In our study, four of the six groups of dyed yellow or "golden" samples could be detected through conventional microscopic observation. Concentrated dye residues and uneven color distribution provided definitive evidence. These products are usually treated after drilling, which was confirmed by the dye residue within and around the drill holes. The other two groups (DSS and DAK) had relatively clean surfaces, and even a trained gemologist would have difficulty in separating them from naturally colored samples. Cultured pearls from the DSS group were treated without the aid of drill holes, while samples from the DAK group were dyed either before or after drilling. If they were dyed after drilling, further treatment such as bleaching may have been used to lighten any color concentrations that accumulated near the drill holes.

All the yellow or "golden" cultured pearls showed decreasing reflectance in the violet/blue region of the visible spectrum, which corresponds with the color reflected, in accordance with complementary color theory and human color perception. But naturally colored samples displayed a gradual decrease in reflectance, with subtle local reflectance troughs at

BOX A: CHARACTERISTICS OF HEAT-TREATED SAMPLES

The three reportedly heat-treated cultured pearls ranged from light yellow to yellow, with various surface characteristics (figure A-1). In one of them, we observed color concentrations similar to those expected in dyed samples.

While their UV-Vis spectra differed from those of dyed cultured pearls in this study (figure A-2), they showed significantly higher PL properties than naturally colored samples tested under the same conditions (figure A-3).

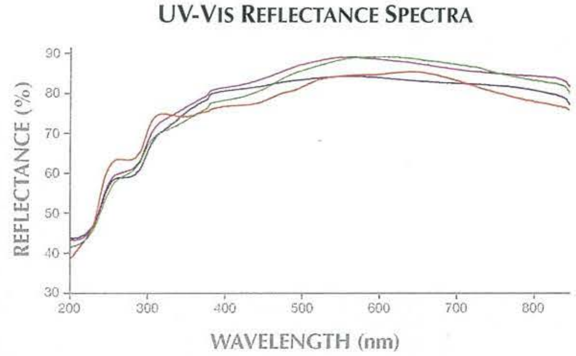


Figure A-2. The UV-Vis reflectance spectra of one naturally colored sample (red) differed from that of three heat-treated yellow cultured pearls.

Figure A-1. These three reportedly heat-treated cultured pearls (top left) show various surface characteristics: even light yellow color with no obvious color concentration (top right), patchy yellow color with obvious orangy concentrations observed at blemishes (bottom left), and even yellow color with no obvious concentration (bottom right).

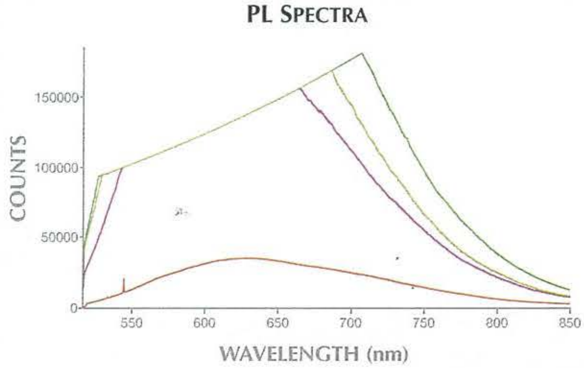


Figure A-3. The PL spectra of the three heat-treated samples show more complete saturation (no Raman signal) than the naturally colored sample (red) under the same conditions, due to their excessive fluorescence signal.

350 and 440 nm, while five of the six dyed groups showed significant reflectance troughs between 410 and 450 nm. These distinct reflectance characteristics can be explained by the different reflectance properties of natural pigments and the predominantly single-component artificial dyes applied to the treated products, as well as the variable concentrations of either. Interestingly, the origin of the golden color found in South Sea cultured pearls may also be derived from nano-composite structures of the nacre, as reported by Snow (2004), which helps further explain the different reflectance features between naturally colored and dyed cultured pearls. For the DFW group, no significant differences were found in the violet/blue region of the visible spectrum, in part because they contained less dye than the other groups. Some of the dyed groups also lacked the local reflectance trough at 350 nm, which occurs almost exclusively in cultured pearls with yellowish hues and may be attributed to a particular pigment.

Although some previous studies have reported the presence of natural pigments in naturally colored freshwater, Tahitian, and *Pteria* species samples (Karampelas et al., 2007; Bersani and Lottici, 2010), our study found no obvious differences using either infrared or Raman spectroscopy. Low pigment or dye concentrations, the location of these materials inside nacre platelets, and strong signal interference by aragonite crystal structure of the pearls could all make it difficult to detect any pigment or dyes using Raman spectroscopy. Yet dyed cultured pearls generally show higher PL under 514 nm laser excitation, likely a consequence of the fluorescence characteristics of the particular dye(s) applied. The result agrees with earlier studies (Liu and Li, 2007; Chen et al., 2009).

CONCLUSIONS

While most dyed yellow or "golden" cultured pearls can still be detected with relative ease using magnification, some show very clean surfaces lacking any evidence of dye. We have demonstrated that these can be identified by nondestructive, advanced instrumental techniques such as UV-Vis reflectance and PL spectroscopy. Our study suggests three indications of dyeing: broad reflectance troughs between 410 and 450 nm, a lack of a reflectance feature at 350 nm, or intense fluorescence in the visible spectrum under 514 nm wavelength laser excitation. When testing cultured pearls using advanced instrumentation, comparative analysis between naturally colored and dyed samples is an important part of the identification process in certain cases. GIA has collected sets of data from numerous naturally colored yellow or "golden" cultured pearls with varying degrees of saturation to use as references for comparison against the spectra of unknown samples. Further analysis of "golden" cultured pearls is needed due to the unlimited number of dye materials that can be used to treat off-color or low-grade goods.

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