University of Nantes
University Diploma in Gemology
DUG English

2017-2018

Experimental Report

Investigation on seven samples of different spieces of cultured pearls, from both saltwater and freshwater origin, to determine the origin of their color

Image of the seven samples, not scale to size

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1. Introduction

I decided to choose pearls as the subject of this experimental report for this DUG course.
The decision was made on this topic as during my last work experience at GGTL laboratories in Balzers, Liechtenstein for Dr. Thomas Hainschwang, I had the opportunity to approach this part of gemology more in depth and I got fascinated form this world that I consider unique for the origin and variety of the natural material that produce.
When I realized that Dr. Stefanos Karampleas was one of the guest invited to give a lecture during the DUG at the University of Nantes last year, I thought that this was a even better opportunity to develop the experimental report in this direction.
With the guidance of Dr. Emmanuel Fritsch the topic was chosen on investigation of colors in pearls.
The University of Nantes loaned me the samples necessary to carry out this project.
The process of writing and drafting this report was quite challenging for me, as without a background in science I found sometimes difficult to direct my work and the analysis of the data in the right orientation.
This course and this report have been a definitely interesting and fulfilling experience, and also a great growing opportunity for me.

2. State of art

The purpose of this report is to conduct various tests on the seven samples in my possession in order to determine the natural or treated origin of their coloration.

3. Material and methods

The present study is based on the measurements of five single pearls and two strands of pearls of various colors (see Table 1 below).
The colors include golden, black, pink, green and light orangish pink.

Table 1:
list of sample description

Sample number	Image of the sample	Number of pieces	Variety	Color description	Color distribution	Shape	Weight in ct / g	Measurements in mm	Details
2164A		1	Hyriopsis FWCP beadless	light orange	even	button	5.14 ct	9.52 x 9.24 x 7.71	half drilled
2165A		1	Hyriopsis FWCP beadless	light orangish pink	even	round	1.08 ct	5.50 x 5.39 x 5.36	drilled
2172A		1	Pinctada Margaritifera FWCP beaded	black-gray	even	round	9.27 ct	10.86 x 10.80 x 10.76	half drilled, containing the metal pin
2175		1	Pinctada Maxima SWCP	golden	even	round	26.08 ct	15.51 x 15.49 x 15.26	half drilled, containing the metal pin, glue stick around the drill hole
2176		1	Pinctada Maxima SWCP	white displaying some iridescence	even	round	23.47 ct	14.88 x 14.83 x 14.58	half drilled, containing the metal pin
3129		104	FWCP	green	uneven, concentrated on drill holes	baroque	8.96 g	from 3.21 x 4.07 x 4.59 to 3.08 x 3.89 x 6.10	drilled and set in a cord strand
3130		36	FWCP	pink	uneven, concentrated on drill holes	baroque	2.18 g	from 2.06 x 3.66 x 3.82 to 2.42 x 3.89 x 4.58	drilled and set in a cord strand

The samples range from 2.06 to 15.51 mm in diameter.
All the samples are property of the University of Nantes and were loaned by Dr Emmanuel Fritsch in November 2017.
The identification numbers of the samples correspond to the codes already given by the University.
The specimens represent only the category of cultured pearls, from both freshwater and saltwater origin, both beaded and non beaded.
Two of the five loose pearls were presented as *P. maxima* saltwater cultured pearls (SWCP), and one as *P. margaritifera* saltwater cultured pearl.

The remaining two loose pearls were presented as *Hyriopsis* freshwater cultured pearls (FWCP).
No particular description on the species was given on the two strands of freshwater cultured pearls.

The 2 strands and 1 freshwater cultured pearl are drilled, while the other 4 pearls are half-drilled with 3 of them still containing the metal pin.
Tests were carried out in two separate sessions.
The first session took place during the month of November 2017 at the IMN (Institut des Matériaux Jean Rouxel) at the University of Nantes, France, with Dr. Emmanuel Fritsch.
The second session was carried out at GGTL Gemlab Laboratory in Balzers, Liechtenstein on the 9th March 2018 with Dr. Thomas Hainschwang.

At first, in Nantes, all pearls were examined with a standard binocular gemological microscope equipped with fiber optic lighting.
The samples' ultraviolet (UV) fluorescence was observed in a darkened room using a long-and short-wave (365 and 254 nm, respectively) UV lamp.
UV-Vis-Nir was performed with a Perkin-Elmer Lambda 1050, with InGAs integrated sphere accessory and spectra were obtained for the 250 to 860 nm range.
Raman spectroscopy was performed with a Burker MultiRam in the range of 100-1200 cm-1.

A T64000 Horiba was also used and spectra were taken in the range between 150-1600 cm-1 and for the two strand of pearls in the range of 150-4000 cm-1.
All the results of the tests in Nantes were saved as .txt, .dpt, .asc, and later converted in Excel files. The images presented in this report are the results of the conversion to Excel.

Measurements and weights of the samples were taken at GGTL Gemlab Laboratory in Balzers, where also x-ray digital radiography was performed using a prototype composed by a high quality ICM X ray tube providing 40 to 120 kV X rays, and a high resolution digital detector providing >20 lp/mm resolution. Images were recorded using an automated rotation device to provide a three dimensional view of analysed samples with much lower image noise and better contrast.
The radiograph of the samples were taken between 60 and 80 kV.
Radiographs of the loose pearls were taken with the rotation device, for a total of 100 images for each pearl, which were then assembled using Photoshop in groups of five images in order to obtain a more clear picture.
Radiographs of the two strand of pearls were taken by placing the strand on the film layer and taking five scan for each position for the same reason as above.

Energy-dispersive X-ray fluorescence (EDXRF) analysis was performed with a Amptek EDXRF system with X ray source providing max. 50 kV X rays and thermoelectrically cooled fast SDD detector, aluminium filter used for X ray tube.
Spectra were acquired with 25 kV X rays, in air.
The spectra images present in this report are screenshot of the results presented by the computer used at GGTL.

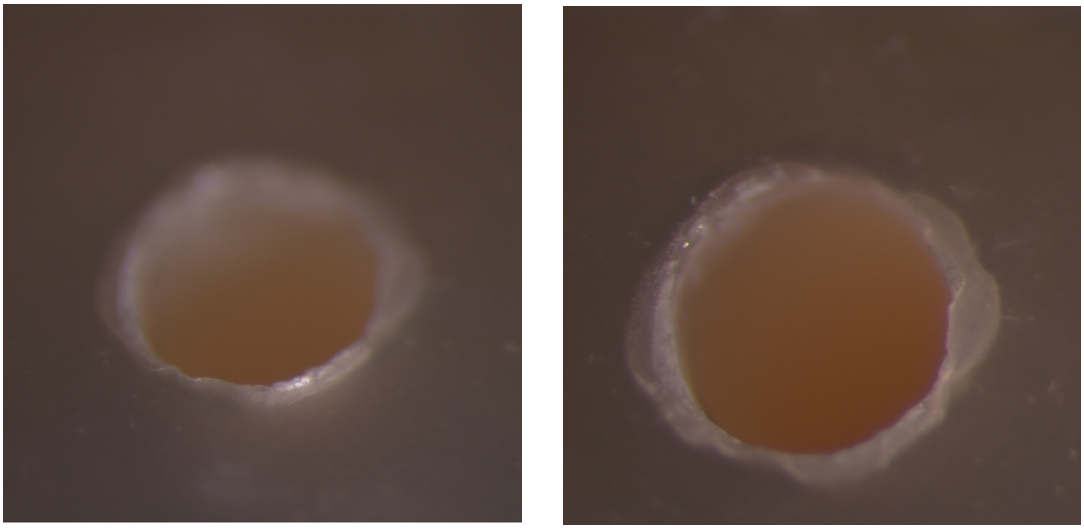
UV-Vis-NIR was taken using a GGTL DC-3 UV-Vis-NIR spectrometer system using xenon, halogen and LED light sources, and a four channel spectrometer with thermoelectrically cooled CCD detectors covering 240 to 1050 nm at a spectral resolution of 0.3 nm. Samples were measured inside a spectralon integrating sphere, in a reflectance setup.

It was not possible to perform UV-Vis on all the sample at the IMN in Nantes so the results shown in this report are the spectra taken at GGTL Gemlab in Balzers, which were converted with the program SpectraGryph.

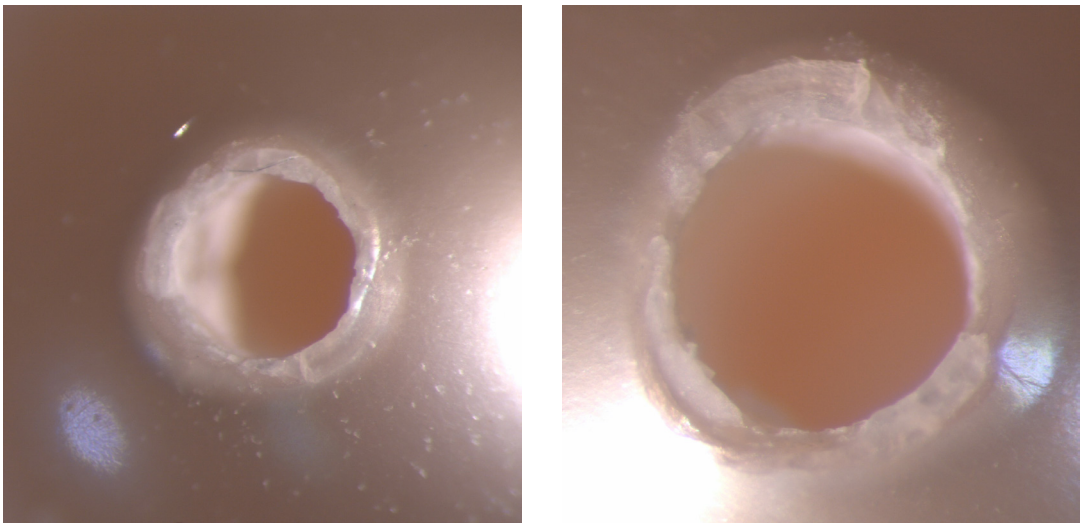
4. Results

Examination of the area around the drill holes of the samples showed the presence of a metal pin in 3 of the 5 loose pearls (see figures 5, 8, 9, 11) and the presence of some sort of glue on one area of sample 2175.
While observing the drill holes of the loose pearls no anomalous coloration was noticed.
Under magnification the two strands of colored pearls revealed a color concentration around the drill holes, and some pearls of the sample 3130 presented pink residue concentrated in quite large pits adjacent to the drill holes (see figures 16 to 31).

Figures 1 and 2

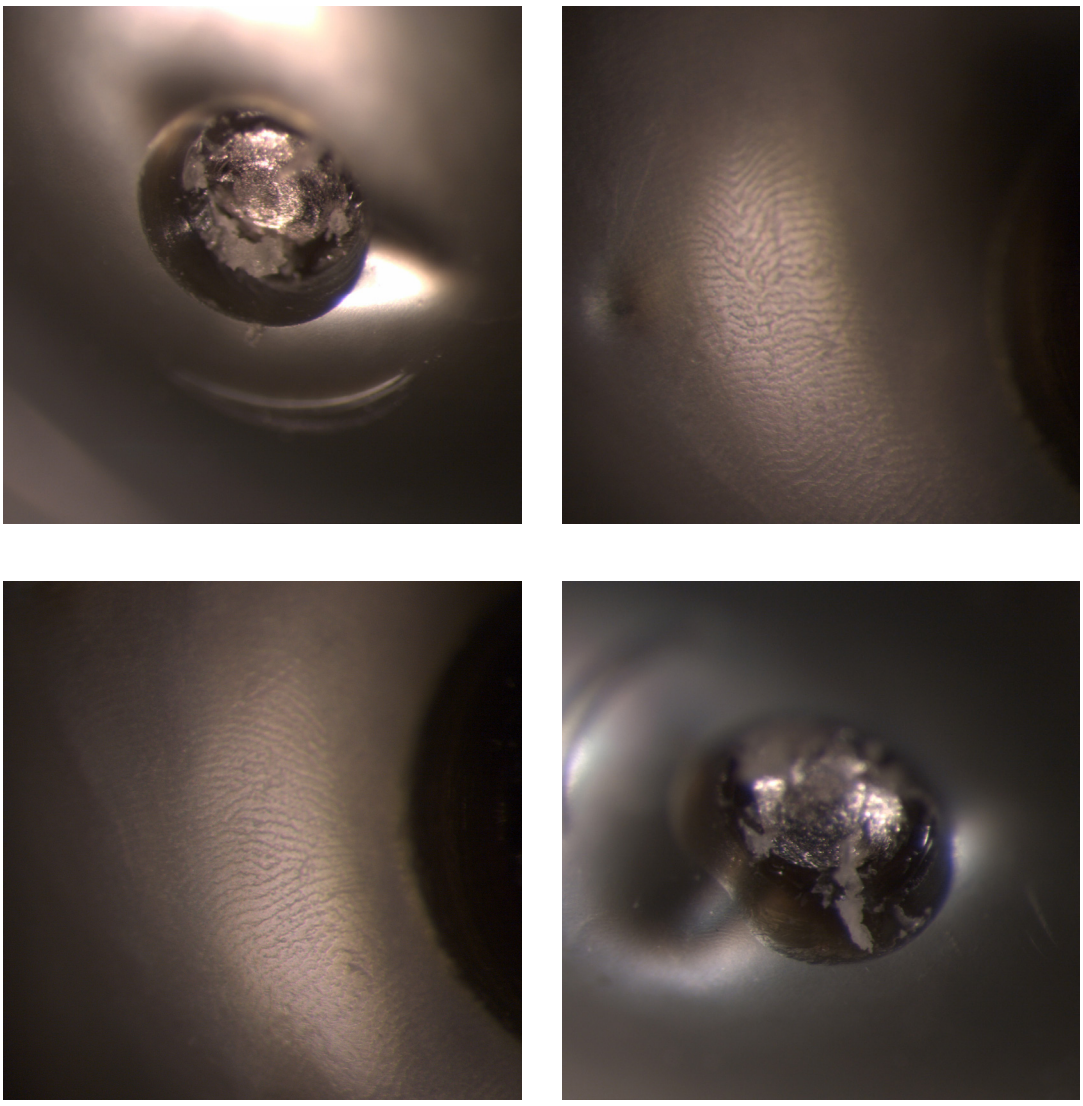


Figures 3 and 4

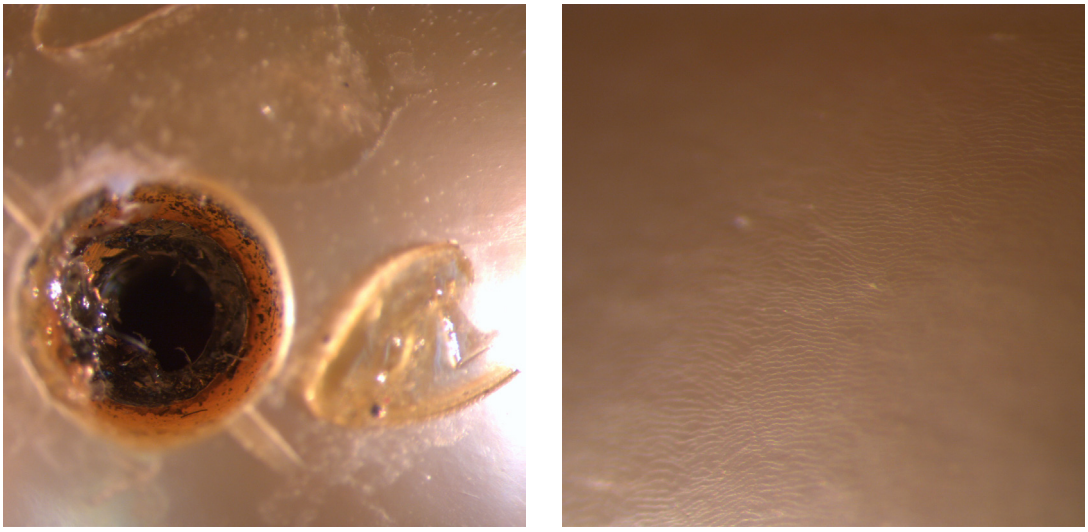


Figures 1 and 2: magnified images of the drill hole of sample 2164A
Figures 3 and 4: magnified images of the drill hole of sample 2165A

Figures 5 to 8:

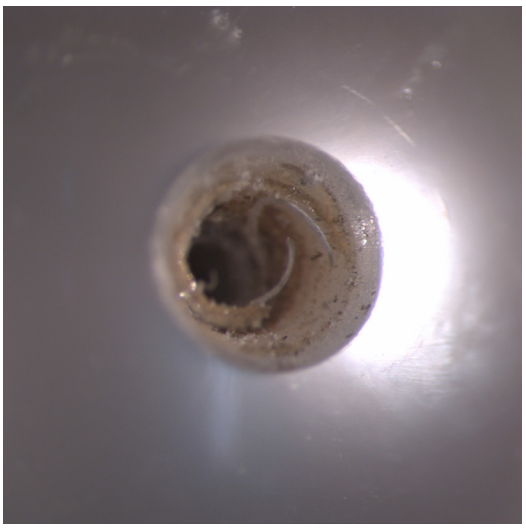


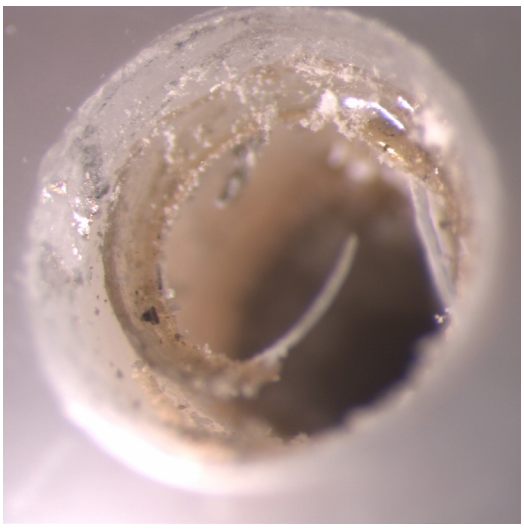
Figures 9 to 10:

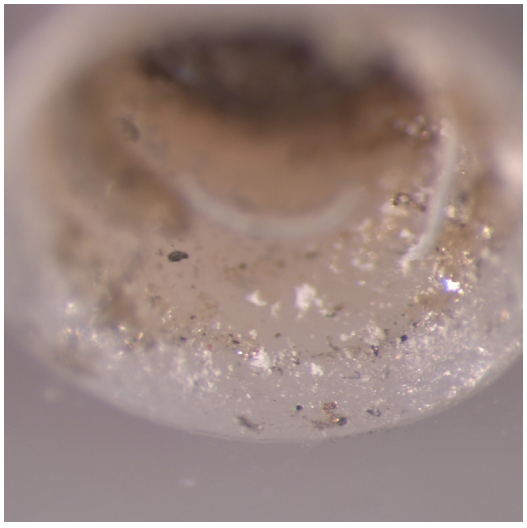


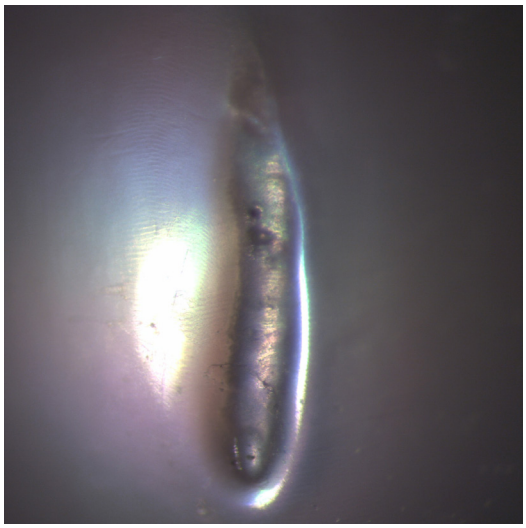
Figures 5 to 8: magnified images of sample 2172A
Figures 9 to 10: magnified images of sample 2175

Figures 11 to 15



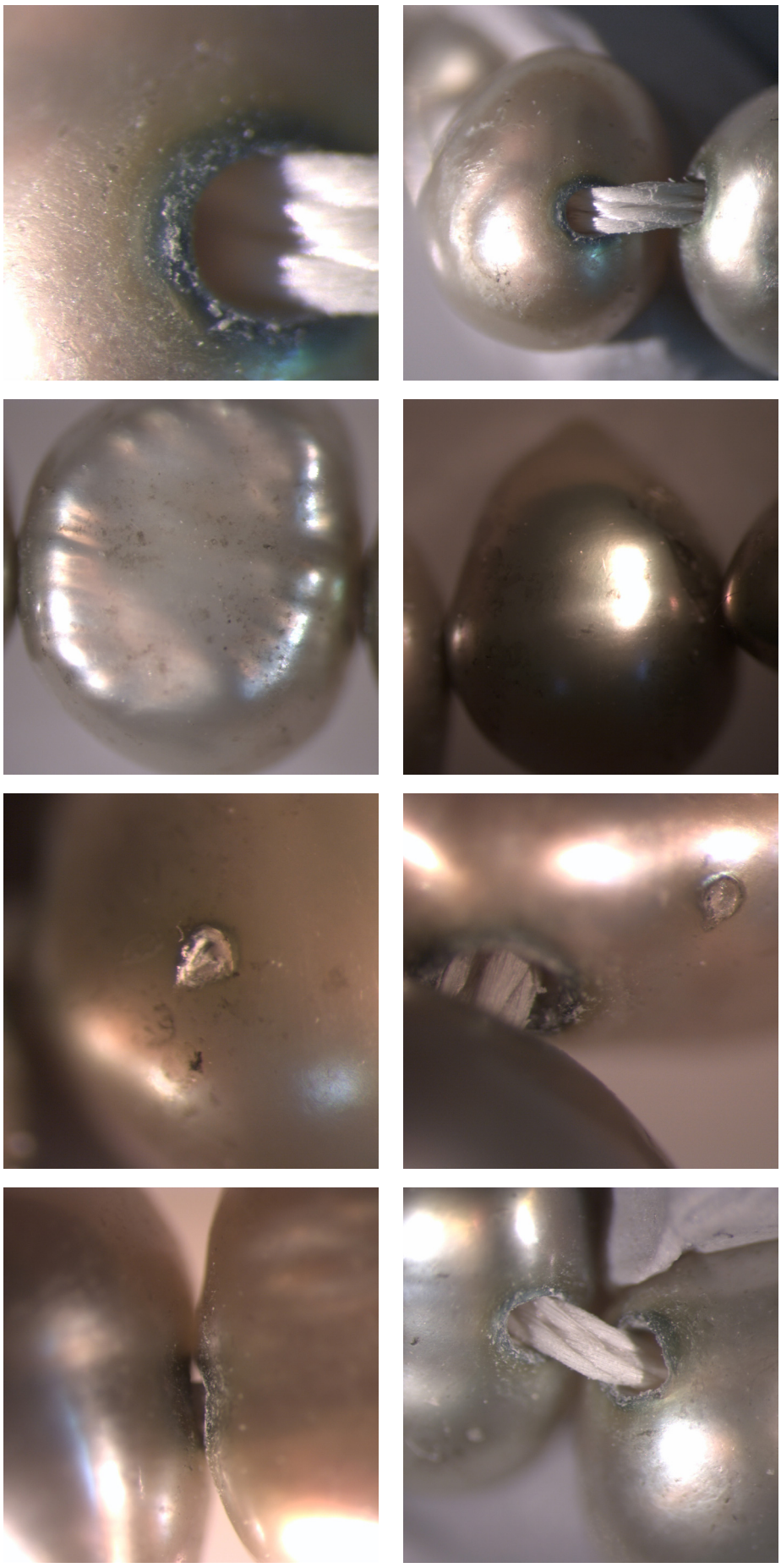






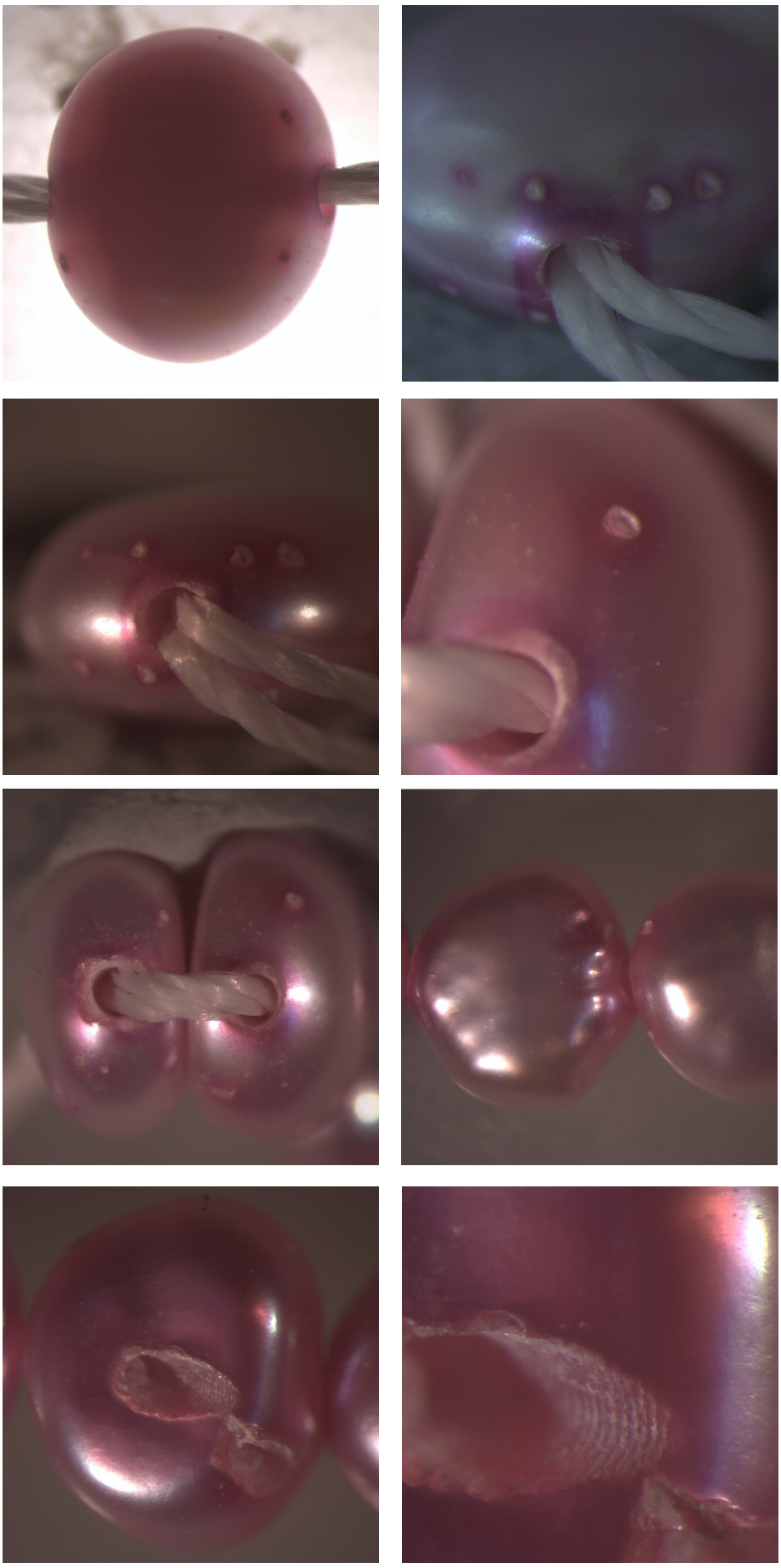
Figures 11 to 15: magnified images of sample 2176

Figures 16 to 23



Figures 16 to 23: magnified images of sample 3129

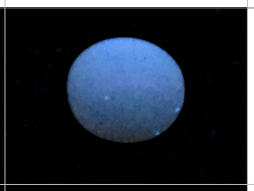
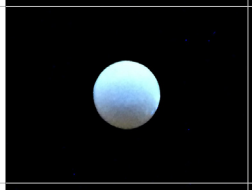
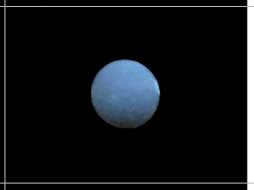
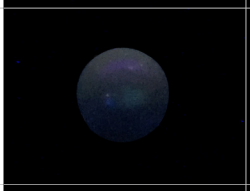
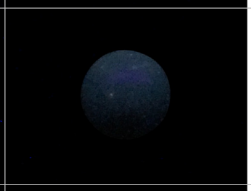
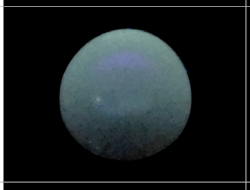
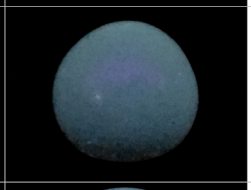
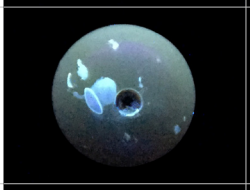
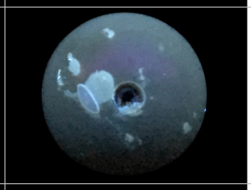
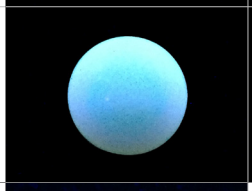
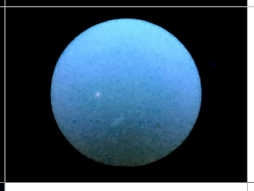
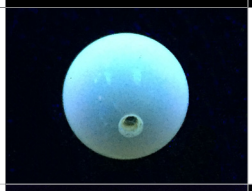
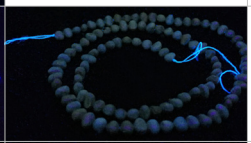
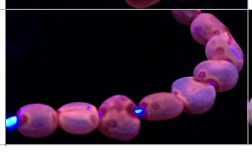
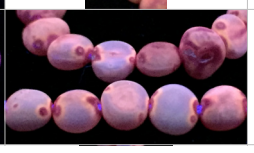
Figures 24 to 31



Figures 24 to 31: magnified images of sample 3130

Fluorescence reaction are shown in Table 2 below.

Table 2:
list of the samples' fluorescence reaction

Sample number	LW image	SW image	LW description (intensity, color, distribution)	LW Phosphore scence	SW description (intensity, color, distribution)	SW Phosphore scence
2164A			medium light yellow even	none	faint light brown even	none
2165A			medium light yellow even	none	faint light brownish even	none
2172A			faint dark red orange even but some patches visible around drill hole	none	faint dark brown green even but some patches visible around drill hole	none
2175			medium dark gold even	none	medium dark gold even	none
			patches around the drill hole due to some kind of glue		patches around the drill hole due to some kind of glue	
2176			strong yellow green even	~ 2 seconds	faint pale white even	~ 2 seconds
			small patches around the drill hole			
3129			medium dark green not even	none	faint dark green not even	~ 2 seconds
3130			strong pink orange not even visible uneven color distribution	none	strong orange not even visible uneven color distribution	none
			visible uneven color distribution		visible uneven color distribution	

EDXRF analysis reveled the presence of phosphorus, calcium and strontium in all samples. Manganese was present in 4 of the samples, (2164A, 2165A, 3129, 3130).
The other 3 samples (2172A, 2175, 2176) did not show any presence of manganese.
Sample 3129 presented small amount of zinc, and the 3 saltwater pearls presented small amount of nickel.

Figure 32

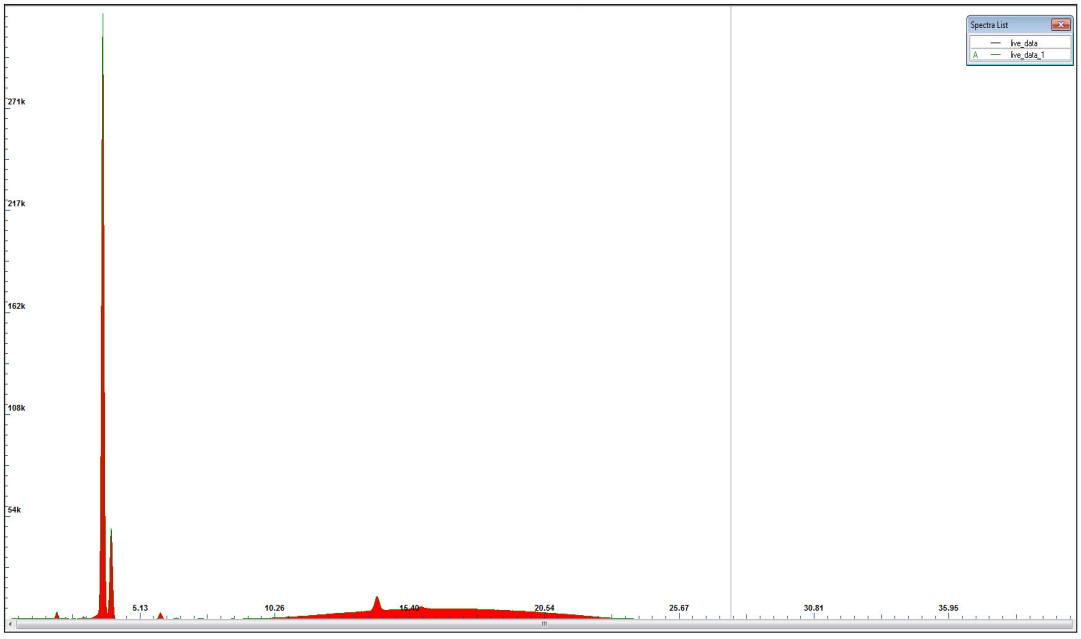


Figure 33

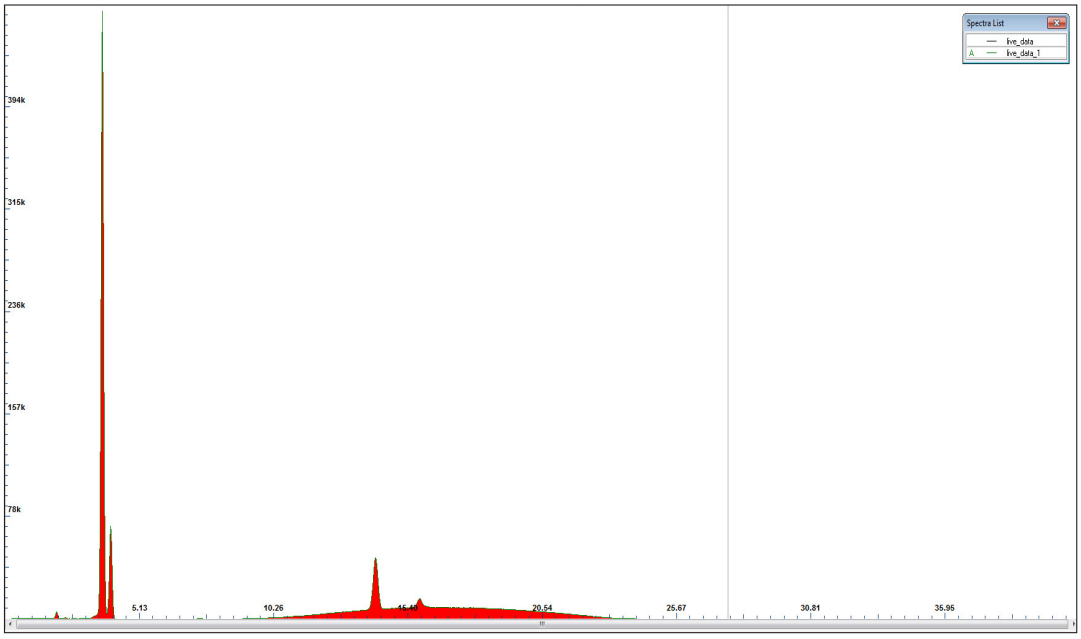


Figure 32: EDXRF spectrum of sample 2165A. This pearl presented the higest content of manganese between the 4 samples found having amount of the chemical element
Figure 33: EDXRF spectrum of sample 2176, presenting small amount of nickel

X-ray radiographs showed the absence of a bead in the two *Hyriopsis* samples.
It is possibile to notice the structure of the donor tissue close to the center of these pearls in the x-ray images.
In one of the sample (2165A) the drill hole pass through the area where the tissue is visible, this results in a not very clear image, but the tissue area is indicated by a red arrow in figure 35.
It is instead possibile to see the bead in the saltwater sample of *P. margaritifera*, and in the two samples of *P. maxima*.
The *P. margaritifera* pearl has a thin layer surrounding the bead, while the two samples of *P. maxima* present a much larger layer.
Sample 2176 showed parallel striation in the area of the bead (see figure 38).
The two strand of pearls present the typical outline of beadless cultured pearls, as shown in figures 39 and 40.

Figure 34

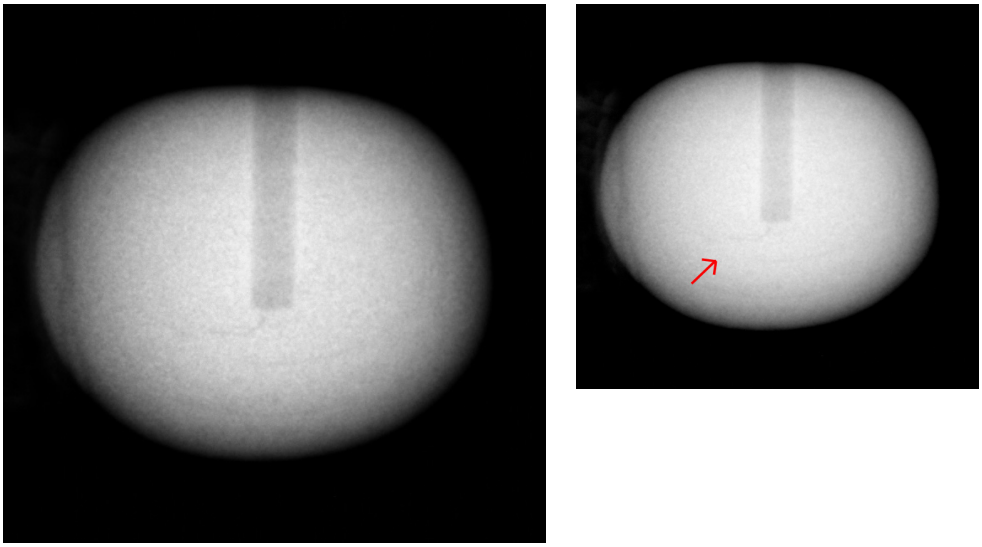


Figure 35

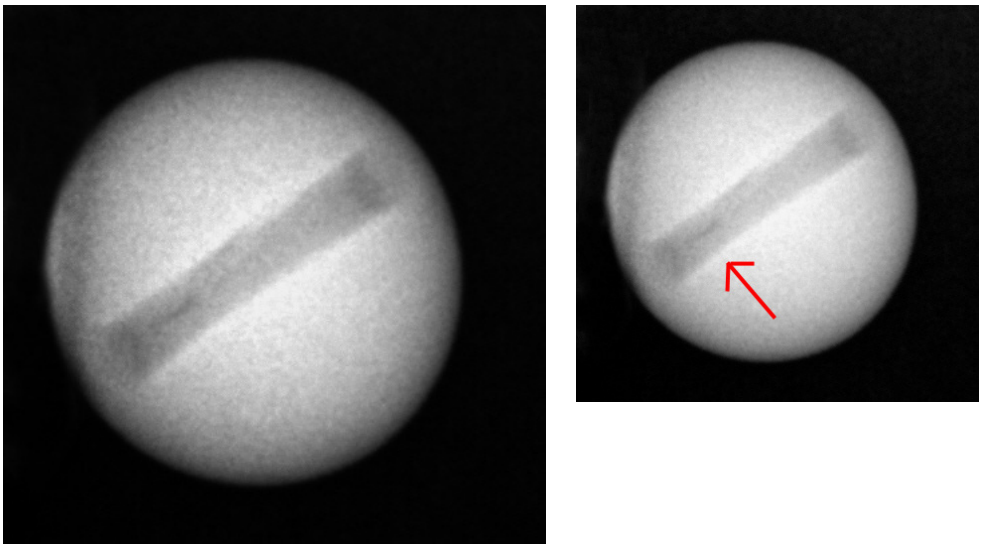


Figure 34: X-ray radiographs of sample 2164A showing the structure of the donor tissue
Figure 35: X-ray radiographs of sample 2165A showing the structure of the donor tissue

Figure 36

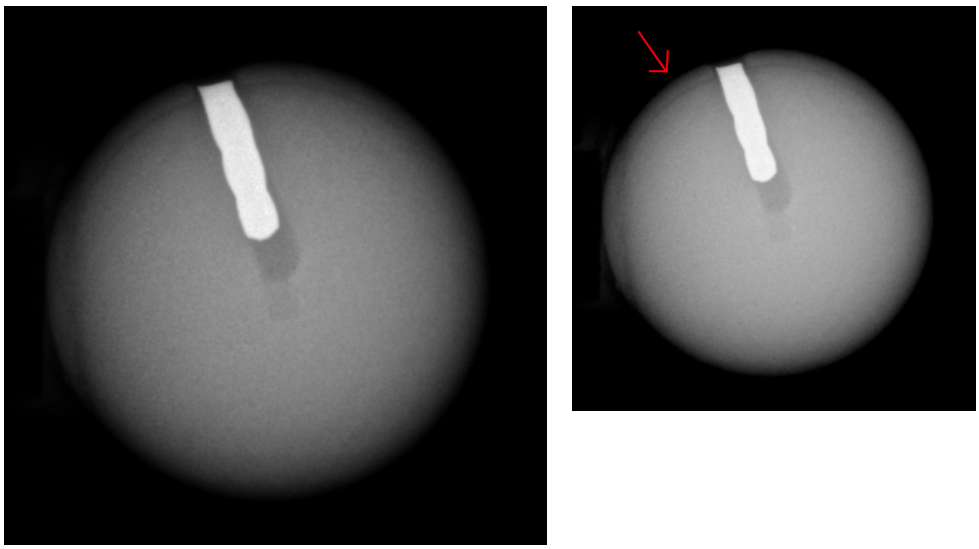


Figure 37

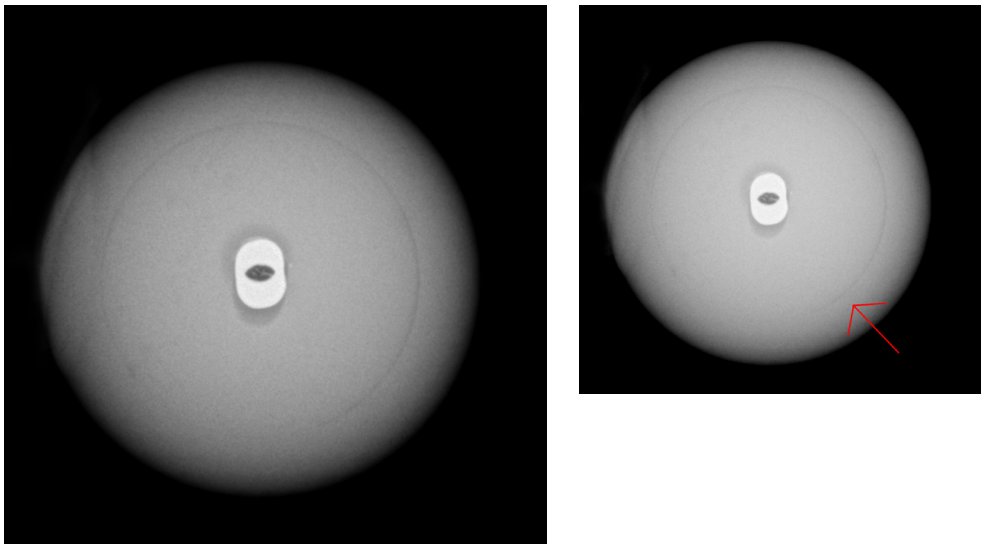


Figure 38

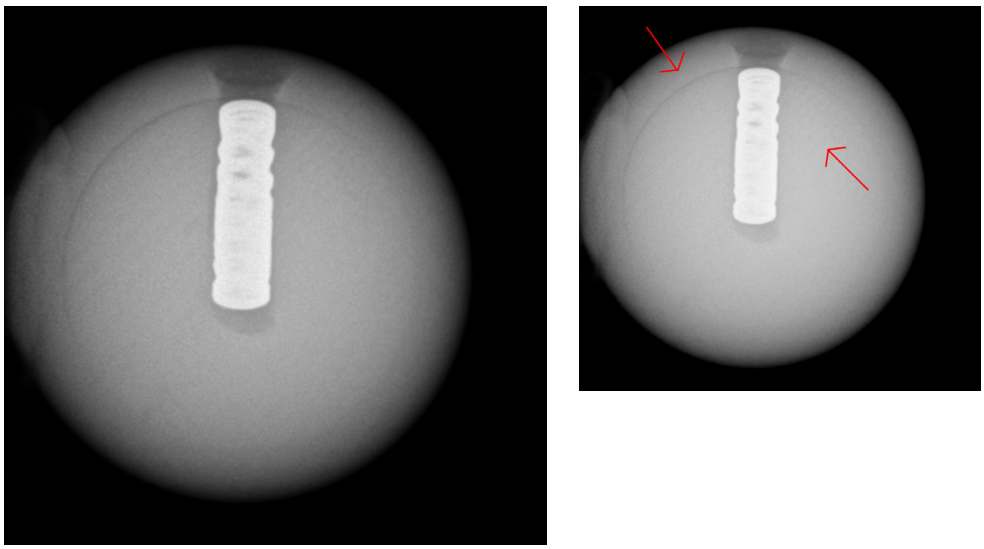


Figure 36: X-ray radiographs of sample 2172A showing the bead
Figure 37: X-ray radiographs of sample 2175
Figure 38: X-ray radiographs of sample 2176, showing parallel striation

Figure 39

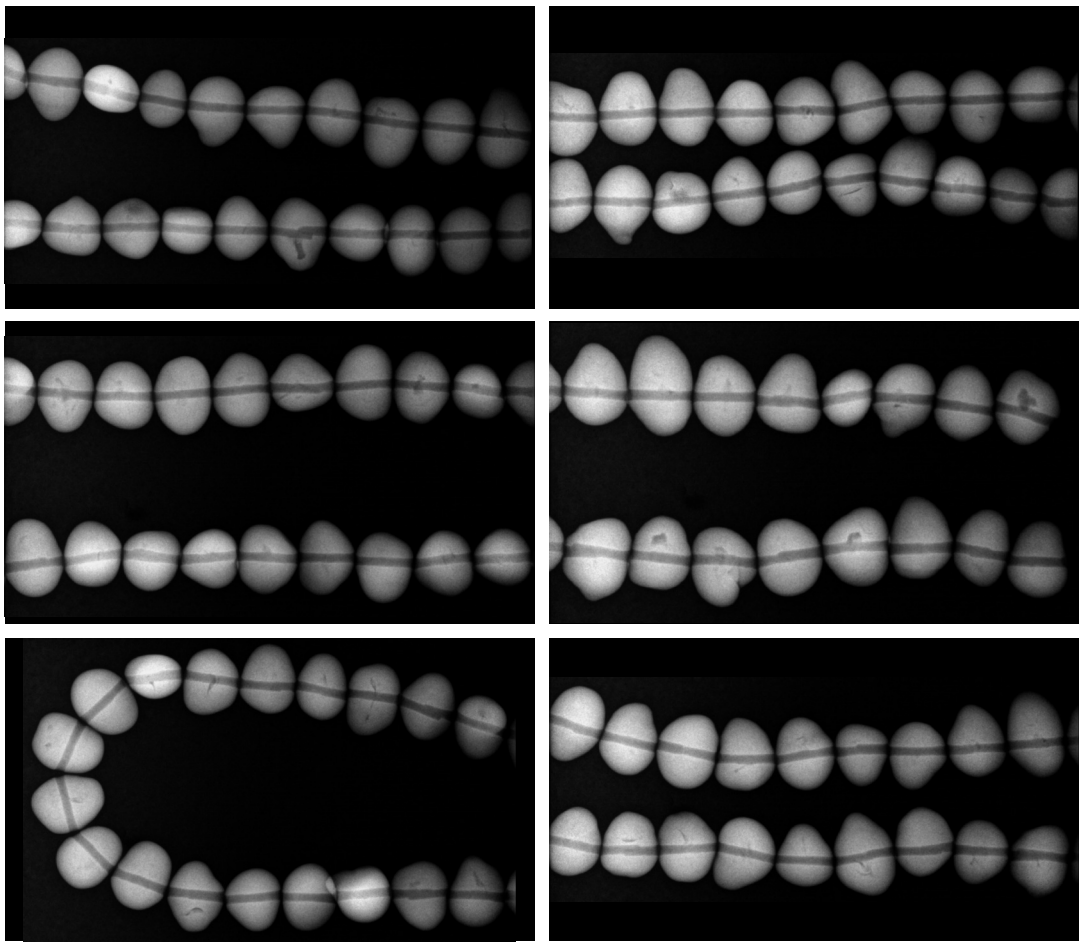


Figure 40

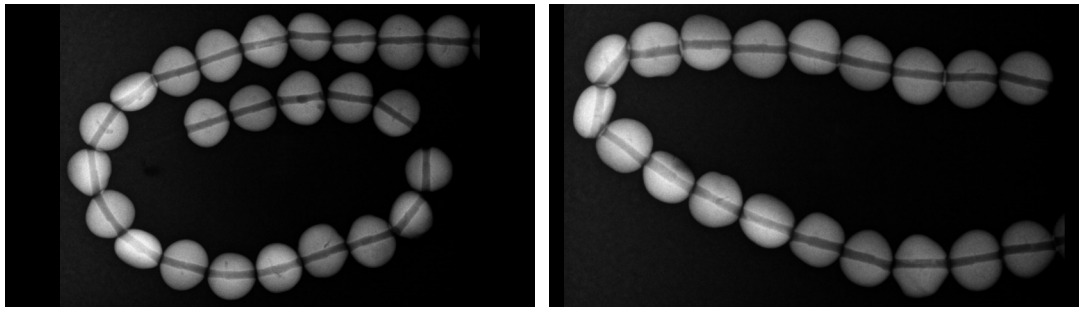


Figure 39: X-ray radiographs of sample 3129
Figure 40: X-ray radiographs of sample 3130

Raman spectra taken with Burker MultiRam in the range between 100-1200 cm-1 of all the samples showed the aragonite peaks at around 1085, 705 and 151 cm-1.

Figure 41

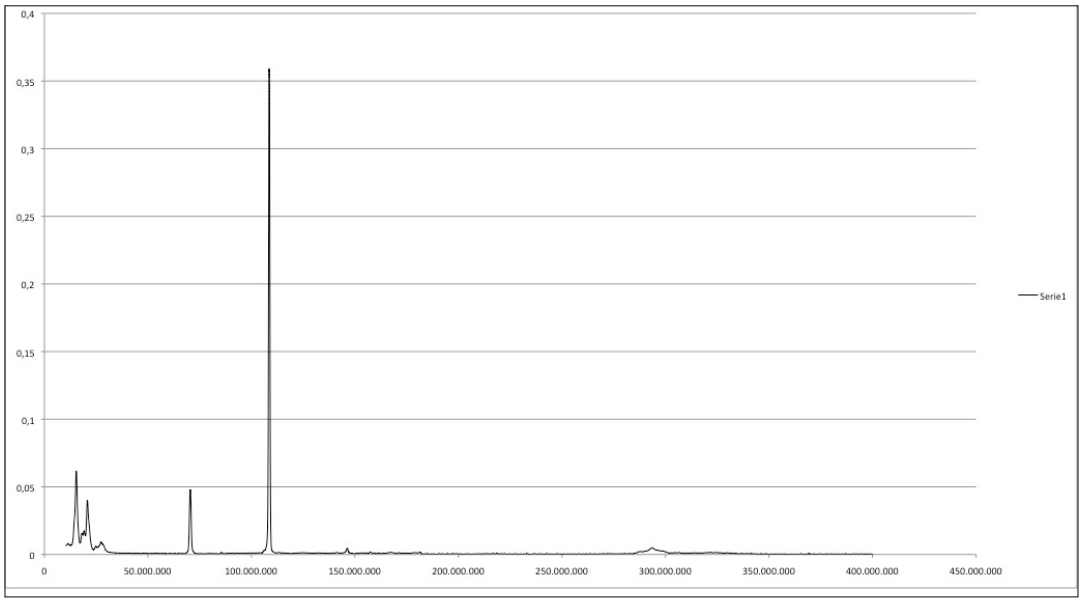


Figure 42

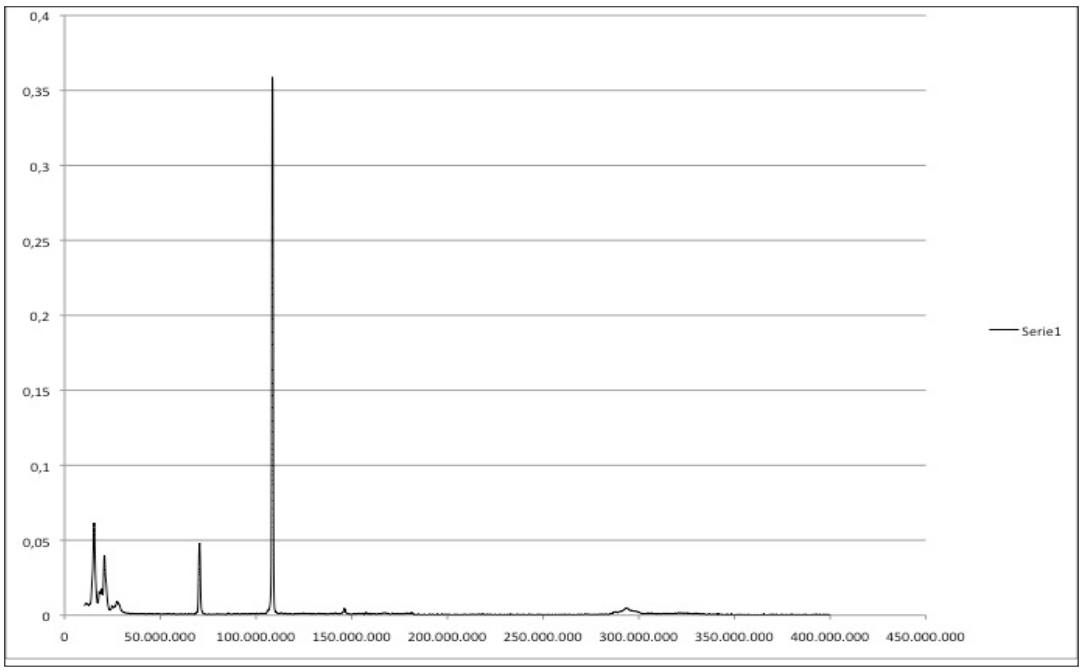


Figure 41: Raman spectrum of the light orangish sample 2164A, *Hyriopsis* FWCP
Figure 42: Raman spectrum of one bead of the green FWCP pearls strand 3129

The spectra taken with T64000 display different features, but all the samples present a double peak at 701 and 705 nm and a peak at 1085 nm from the aragonite.
The results from the two samples of *Hyriopsis* show two small peaks at around 1130 cm-1 and 1530 cm-1, which are more prominent in sample 2165A (see figure 43).
For the two strands of colored pearls, spectra were taken for at least three different beads.
In this report is shown only the spectra of one bead for each of the two samples.

Figure 43

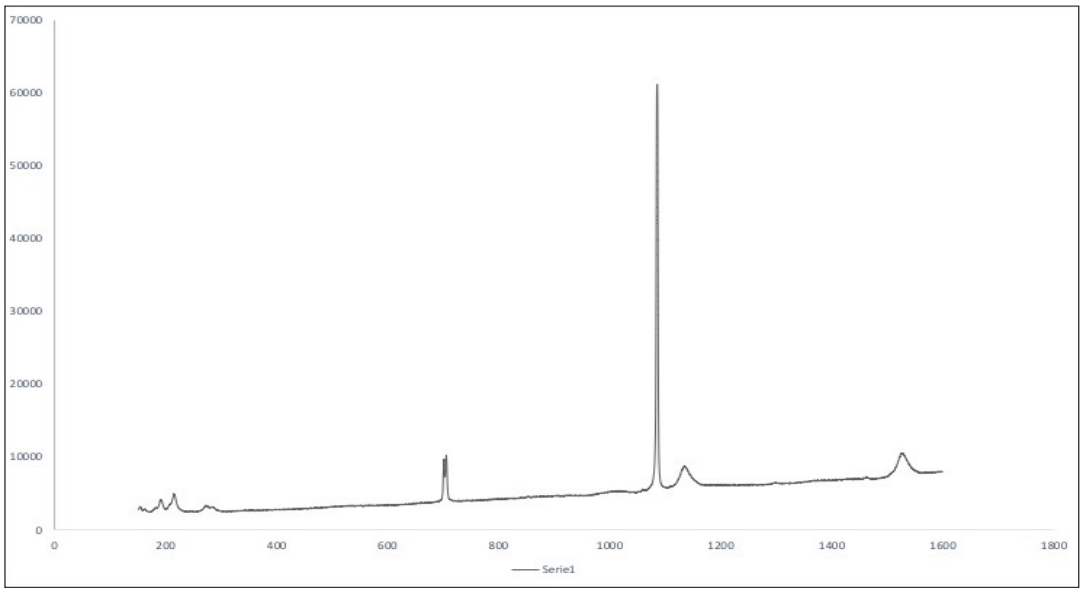


Figure 44

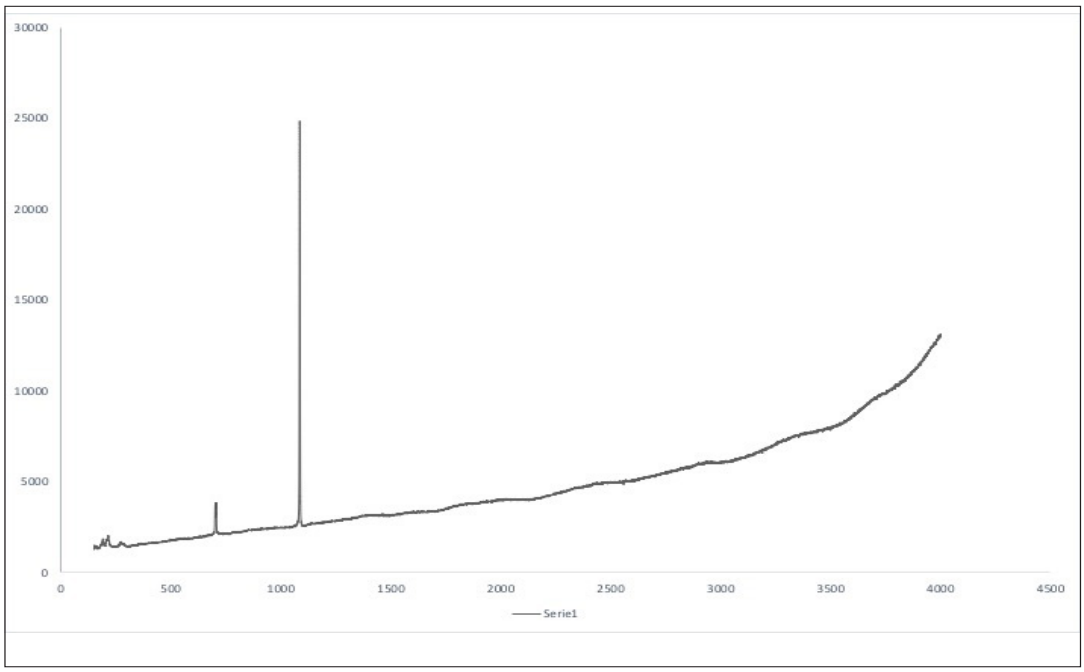
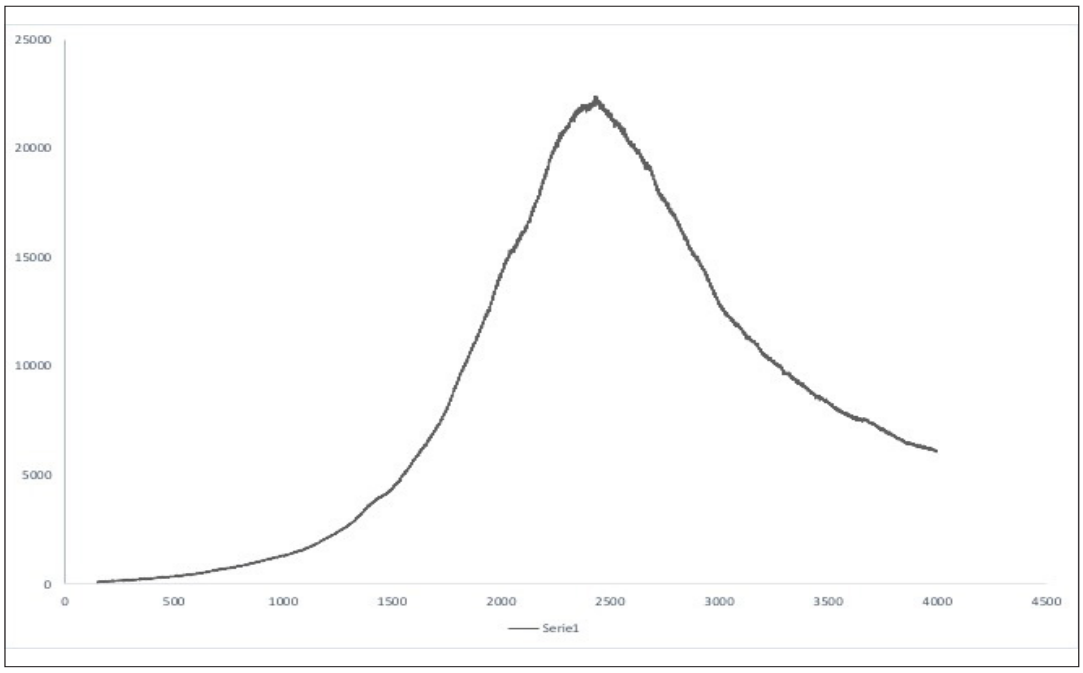


Figure 43: Raman spectrum of the *Hyriopsis* FWCP sample 2165A, showing peaks at 1130 cm-1 and 1530 cm-1
Figure 44: Raman spectrum of the green strand of FWCP, sample 3129

Figure 45



Figures 46-52 show the UV-Vis reflectance spectra of all the samples, all the spectra revealed a decrease in diffuse reflectance due to absorption in the ultraviolet range at 280 nm.
Figure 46 shows the UV-Vis-NIR spectrum of the light orange *Hyriopsis* pearl (2164A).
An absorption at around 280 nm is visibile, together with a strasmission around 400 nm.
A quite similar spectrum is presented in figure 47, of the light orangish pink *Hyriopsis* (2165A), with the addition of a transmission band from around 850 to 1000 nm.
Figure 48 shows the spectrum of the *P. margaritifera* black sample 2172A.
Absorptions at 280, 405, 495 and 700 nm are visible together with transmission between 500 and 650 nm. The black color occur because all the absorptions are equally intense.
The spectrum of the *P. maxima* sample 2175, presents a broad absorption band from around 330 to around 460 nm, which is observed in yellow to golden natural color samples from *P. maxima* (figure 49).
2176 shows that the light of the visible part of the spectrum (390-780 nm) is transmitted, in agreement with the white color.
Figure 51 shows the spectrum of the strand of green colored pearls, where transmission at 500-550 nm and absorption at 600-700 nm are the cause of the green coloration.

Absorptions at 280 nm is visible in the strand of pink colored pearls, transmission between 410 and 500 nm, and absorption around 570 nm is present (figure 52).

Figure 45: Raman spectrum of the pink strand of FWCP, sample 3130

Figure 46

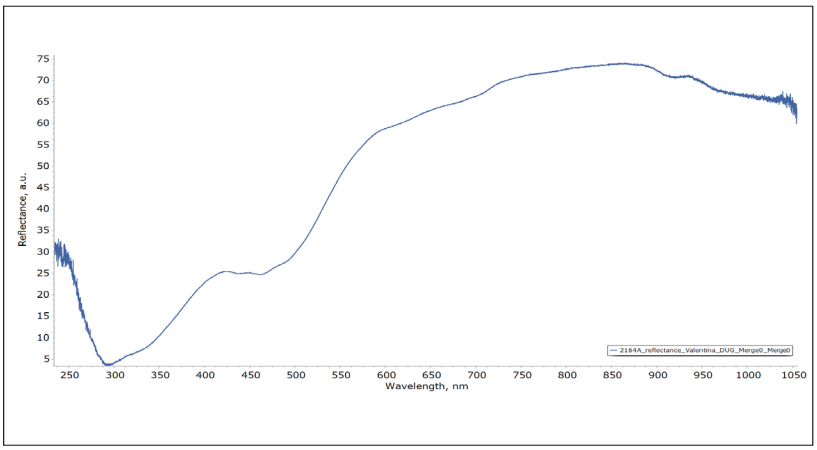


Figure 47

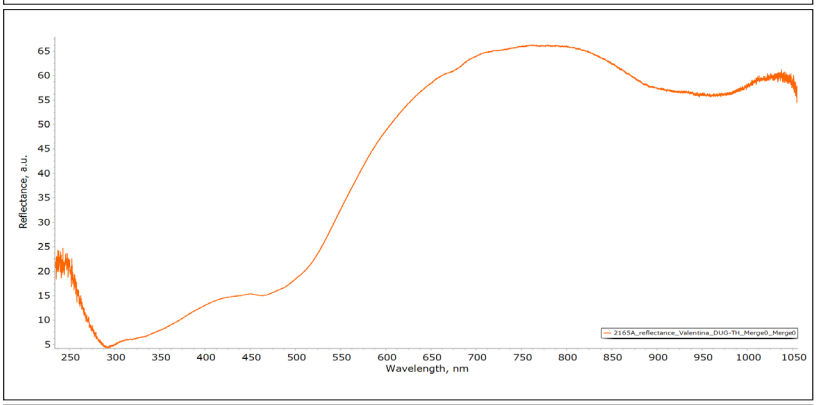


Figure 48

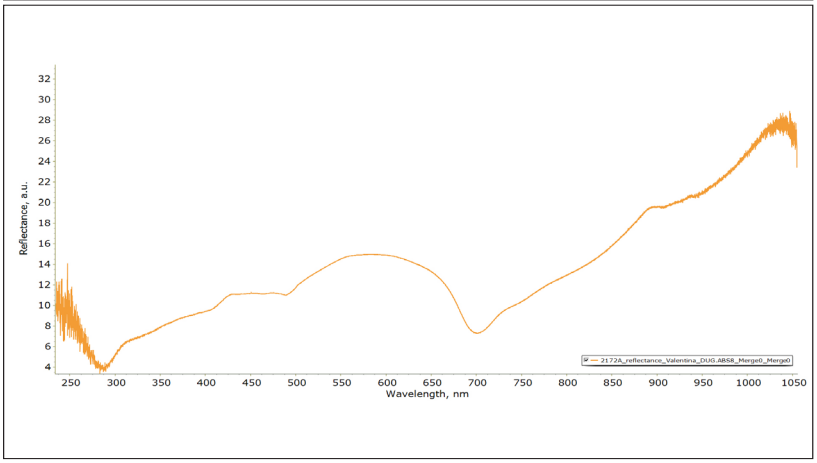


Figure 49

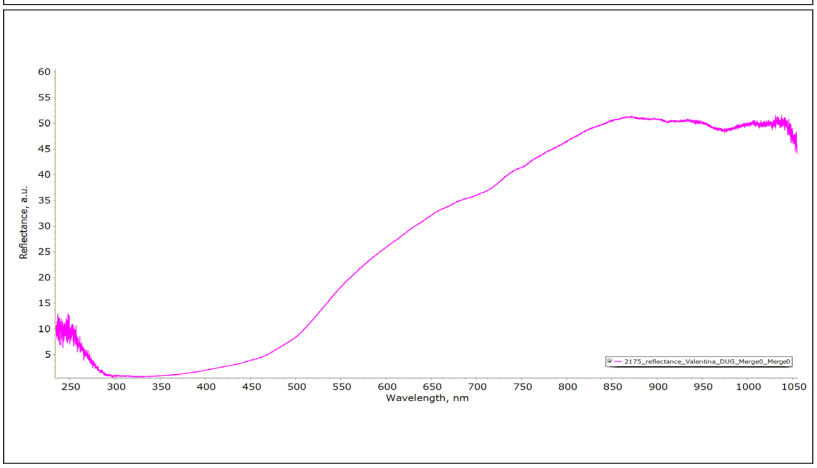


Figure 46: UV-Vis of sample 2164A
Figure 47: UV-Vis of sample 2165A
Figure 48: UV-Vis of sample 2172A
Figure 49: UV-Vis of sample 2175

Figure 50

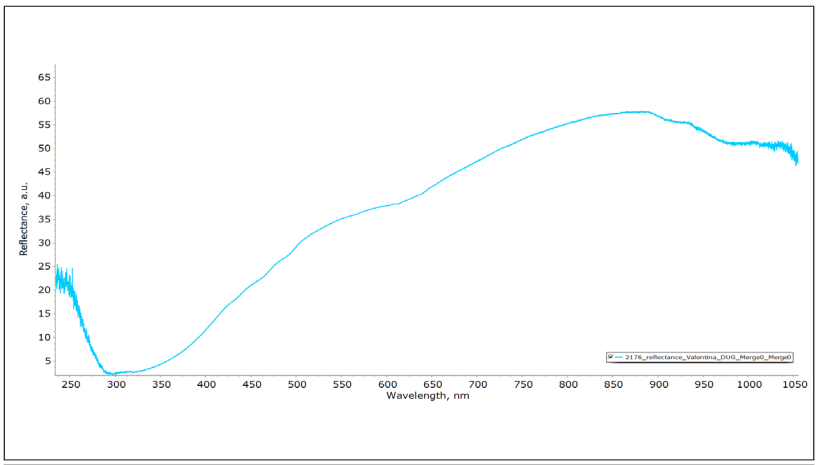


Figure 51

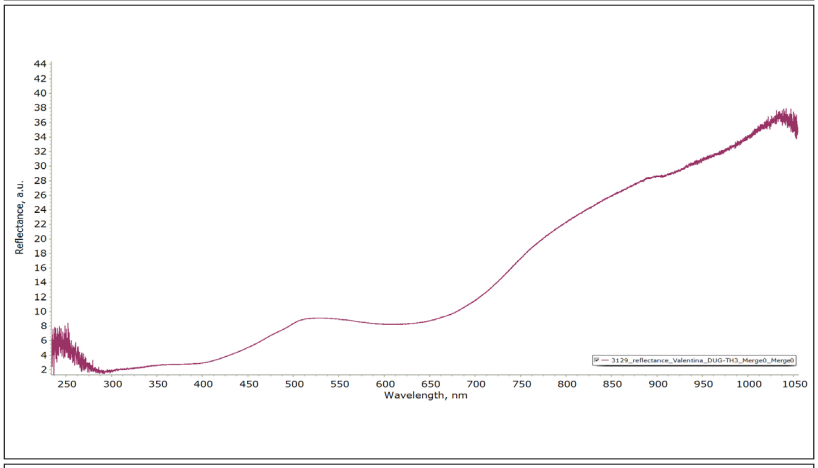


Figure 51

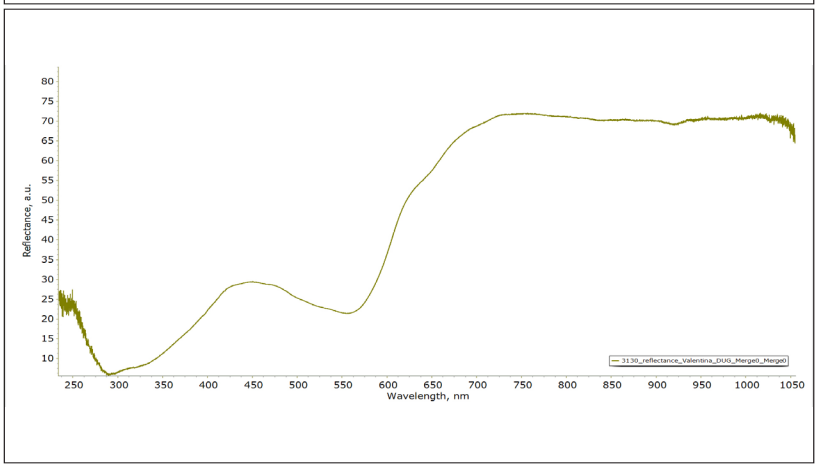


Figure 50: UV-Vis of sample 2176
Figure 51: UV-Vis of sample 3129
Figure 52: UV-Vis of sample 3130

5. Discussion

The color of cultured freshwater pearls of the *Hyriopsis* genus is due to a mixture of short unsubstituted polyenes. Two strong Raman resonant bands, due to polyenic chains, occur in the 1100-1200 and 1450-1600 cm-1 ranges. These bands correspond respectively to the carbon-carbon stretching vibration of a C-C single bond and to that of a C=C double bond in a polyenic chain (Karampelas et al., 2009).
In the spectra of the two *Hyriopsis* samples, 2164A and 2165A, these two bands at around 1130 cm-1 and 1530 cm-1 are visibile and indicate the presences of a mixture of polyacetylenic pigments. These characteristic features suggest the natural origin of the color for these pearls.

In sample 2172A, *P. margaritifera* FWCP of black color, no dye was detected by chemical analysis. This dark coloration is quite characteristic for pearls of this species.
Absorption at 700 nm (as shown in figure 48) in UV-Vis-NIR is typical of natural color, however the origin of the feature at 700 nm and the black pigmentation in this mollusk have not been truly identified yet. Probably are due to the presence of a combination of eumelanin and phaeomelanin or of an unusual type of melanin (Elen S., 2002).
In addition the black *P. margaritifera* FWCP exhibited a characteristic reddish brown fluorescence under long wave UV.
All these features together are suggesting a natural origin of the color of this pearl.

Natural color of *P. maxima* golden cultured pearl could be caused by an absorption feature in UV-Vis-NIR between 330 and 385nm. This feature is generally found in natural color yellow CP (cultured pearl) of this species and not in treated ones. The reason for the color could be a zoochrome, a naturally occurring pigment (Elen S., 2001).
The sample 2175, golden SWCP of *P. maxima*, presents a broad absorption from 330 to 460 nm. The absence of the UV absorption feature in golden cultured pears indicated treated color (Elen S., 2002).
Raman does not show any pigments in golden *P. maxima* colored pearls (Karampelas et al., 2009).

Sample 2176 *P. maxima* white cultured pearl did not show any anomalous feature in the results of the tests that have been carried out.
From what have emerged the assumption is of natural color origin.

Visual observation and Raman scattering of the two strand of pearls (3129, 3130) are indicating that the color of these pearls is originating from a dye.

6. Conclusion

After the analysis of the data collected during the tests carried out on the samples, and through the help of the information contained in the bibliography, I reached the formulation of the hypothesis that samples 2164A and 2165A (*Hyriopsis*), 2172A (*P. margaritifera*), 2175 and 2176 (*P. maxima*) are naturally colored cultured pearls.
While samples 3129 and 3130, FWCP are colored treated, with the color originating from a dye.

7. Aknowledgment

I would like to express my gratitude to Dr. Thomas Hainschwang who gave me access to GGTL Gemlab Laboratory in Balzers, in order to carry out the final tests necessary to create this report.
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And finally to Dr. Emmanuel Fritsch and Dr. Benjamin Rondeau who were a great guidance during this DUG course.

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