RAMAN Scattering: Fingerprint for Identification of nature and color origin of Pearls

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Abstract: *Pearls are the first gems, which are created entirely by nature and do not require human assistance to enhance their beauty, popular since prehistoric time. The color of a pearl is determined genetically by the host mollusc. Laser Raman spectroscopy helps in the identification of the primary matrix, as the external features are the same in all types of pearls. Raman spectroscopy is also used to determine pearl's nature of origin, as to natural, cultured, dyed pearls, irradiated pearls and imitation pearl. Raman scattering is used to detect natural pigments on pearls and in some cases to detect color treatments. All the pearls present the characteristic peaks of aragonite at 702 cm^{-1} (normally a doublet at 701 and 705 cm^{-1} depending on the resolution used) and 1085 cm^{-1}. Natural Colored FWCPs peaks at around 1132 cm^{-1} and 1530 cm^{-1} which are characteristic of polyenic pigments. Color characteristics also differ according to the mother oyster species. The phenomenon of iridescence that shows glittering of various colors in a pearl is due to the interference and diffraction of light interacting with the specific structure on the pearl's surface. Thus an attempt is made on all the above aspects by using the non-destructive method.*

Key words: Pearls, Oyster, Polyenic Pigments, RAMAN Spectroscopy

1. INTRODUCTION

Gems have been symbols of status, power and honor throughout history. King, queen, and nobles have sought to possess them and more often, the beauty of a pearl is something that is not felt by touch but felt by the heart. Pearl is counted among the revered nine gems and has been treasured since the beginning of human civilization. In its purest and original form itself pearl is a beauty adored whereas the rest of the gems are appreciated after they are cut and polished to bring out their beautiful properties [1]. A pearl is hard, rounded organic gem object which is produced by molluscs and oysters. Pearls can be used in jewellery, paints, some of the cosmetics as well as in medicines. Pearls are mentioned even in the earliest of the Indian Vedas. The Rig Veda and the Atharva-Veda states that when the ocean roared against Paranjaya with lightning, the pearl was born as a golden drop from it [2, 3].

The factors that contribute to the color of a pearl includes the type of oyster, the thickness and the number of layers of nacre, and the possible trace elements in the oyster's aquatic environment. Different molluscs produce pearls of different colors. Other factors affecting a pearl's color is the environment in which they are cultured, the trace-elements found in those waters and importantly, the color characteristics of the tissue that is inserted with the bead nucleus during the implant process. Minerals and trace elements in the seawater are essential, as these also influence the color of pearls. Raman scattering is used to detect natural pigments on pearls and in some cases to detect color treatments. To see the color, you need to have the white light. When light shines on an object some colors reflect the object and others are absorbed by it. Our eyes can only see the colors that are bounced off or reflected. All light rays contain color and are made of electromagnetic waves. Color is related to the wavelength of light. If a color corresponds to one particular wavelength, it is called spectral color. Different colors have different wavelengths; the longest wavelength of light that humans can see is red. The shortest is violet [4, 5].

1.2 Background

Pearls are organic gems which are formed by a living creature and a living shelled molluscs that may produce a variety of pearl that is unique to the shell species. Pearl quality is measured by comparing size, shape, color, luster and surface features. Larger, unblemished, lustrous and spherical pearls are considered to be more valuable. Depending on the pearl oyster species, color is a more subjective indicator of value, with white South Sea pearls, especially those with a pink overtone, holding the highest value of any marine pearl with similar quality characteristics [6].

The color of a pearl is determined genetically by the host mollusc. The final color of the pearl can also be affected by water conditions, disease, or nutrient supply. Pearls usually exhibit both body color and an overtone. Body colors include white, silver, cream, yellow (golden), gray, or black. The overtone is like a whisper of color over the body color –

much like powdered blush over makeup. Overtone may be rose, green, blue, or violet. Molluscs live on the sea floor or riverbed and feed on plankton or other organic nutrients suspended in the water. Pearl is unique amongst gem materials. Apart from being drilled, it is mostly worn as it is found; whereas, except for the rare well-formed crystal, diamonds, rubies, sapphires, and emeralds all require cutting and polishing before they are seen at their best. Perhaps because of this, pearls are one of the oldest gems known to man. A pearl is also unusual as a gem material and is growing today in many different parts of the world (China, India Japan, Korea, Vietnam, Red Sea, Australia, New Zealand, Indonesia, Tahiti, Philippines, North and South America, Caribbean, Scotland) [6-9].

1.2.1 Natural Pearl

The pearl is one of the earth's most perfect creations and one of mankind's most treasured gems. Nature alone is responsible for this soft, delicate gem whose beauty and purity has captivated humankind for thousands of years. Pearls are a symbol of purity and feminine charm. A natural pearl is formed when a small irritant (rarely a grain of sand) lodges in the mantle tissue of a mollusc. In response, the mollusc secretes a substance called nacre, and a pearl starts getting formed. Nacre is a combination of crystalline and organic substances. The nacre builds up around the irritant in layers to protect the mollusc. After a few years, this build-up of nacre forms the pearl.

1.2.2 Cultured (manmade) Pearls

Cultured pearls generally are formed the same way as natural pearls, the only difference is that the irritant is surgically implanted by man. Presently over 95% of the world pearl production is cultured. Cultured pearls can be divided into two types of pearls: freshwater pearls and saltwater pearls. As their name implies fresh water pearls are formed in fresh water mussels that live in lakes, rivers, ponds and other fresh water bodies. Most fresh water cultured pearls sold today comes from China. On the other hand, salt water pearls grow in oysters that live in the sea or ocean and in protected lagoons. Akoya, South Sea and Tahitian pearls are the three main types of salt water pearls [2].

1.2.3 Simulant / Imitation

Cultured pearls are cultivated by man but often much better aesthetically. For commercial reasons pearls have been imitated, at least since the mid seventeenth century, as hollow spheres of thin glass coated on the inside with a spherical varnish made from fish scales and usually filled with paraffin or wax .For this reason pearls were once tested between the teeth if they break they were clearly judged as duplicate. They were subsequently imitated by spheres of glass, or mother of pearl, varnished on the outside in the same way. All these imitations are very easily recognizable if observed under a magnifying glass which shows typical fusion around the hole, the paraffin wax filling and the translucent outer layer in one case and in the other, the minutely granular appearance of the special varnish used [10, 11].

1.2.4 Various Treatments on Pearls

The first thing that happens to a pearl during processing is that it is cleaned up. In general the pearls are cleaned up by scrubbing, polishing and bleaching. These processes are trade secrets of each company. Off colored pearls may be dyed. Shades of blue, grey, brown and black are standard shades for dyed in marine water cultured pearls. Some pearls are dyed pink to enhance the overtone. To see if a pearl is tinted pink artificially look around the drilled hole and scrutinize the blemishes. Dyed pearls show a concentration of dye in these areas. To enhance the beauty and luster of pearl, inferior quality pearls are taken into consideration for the further treatments [10, 11].

Drying is an essential operation it removes the small tint of green color peculiar to all freshly harvested pearls. Some pearls have a particular color because of the shellfish which secrete them and the conditions of their gestation. In cases of an excessive secretion of organic material, the pearls produced can have an unpleasant color due to dehydration called as *bleaching*. Silver nitrate has been used for many decades to darken the appearance of the pearls. The chemical penetrates the layer of nacre and has a chemical reaction with light or hydrogen sulfide gas to create a rich black color. To create colors other than black the farmer may also use organic or inorganic dyes to produce another color variation. One disadvantage of this treatment is that the black color might turn brown over time. The *dye* can be observed through the drill hole. *Coating* a pearl to enhance its luster is not widely practiced and is much frowned upon. Although luster may appear to be fine, the coating may eventually chip or peel, leaving a low luster pearl visible beneath the thick surface. Although nearly all the pearls on the market have been treated in some way, it can be challenging to detect pearls treated to change color. One method of detecting dyed or irradiated pearls is to check the matching of the strand. A strand of natural color pearls typically varies slightly from pearl to pearl. By peering down the drill hole of a dyed pearl one may also be able to see concentrations of color. When looking down the drill hole of an irradiated pearl one may be able to detect a darkened nucleus. This is the strong evidence of gamma-ray treatment. Typically a coating is placed on the surface of the pearl to enhance the *luster* artificially. It is much harder to spot. The most basic method, however, is to compare an untreated strand with the suspect strand under at least 50x magnification. The untreated pearl has a scaly nacre surface. The coated pearl will has a smooth glass like surface. The use of gamma rays is done to darken the nucleus of the cultured pearls and the nacre layer in fresh water pearls. *Irradiation* has differing effects from fresh water to salt water cultured pearls. The gamma rays do not affect the nacre layers of salt water cultured pearls but in fact darken the nucleus of the pearl. An irradiated salt water pearls appears to be grey to blue. The nacre of irradiated fresh water pearls; on the other hand, when affected by the gamma rays, can become very dark.

2. LITERATURE REVIEW

As with other gems, pearl value is linked to rarity. Pearls occur in a broad range of hues. In tone, pearls have a wide range, from light to dark. Pearl colors are low in saturation. Due to such quality factors and market value, many of scientists and researchers showed an interest in pearl investigation. Hyatt et, al. [12], presented towards the goal to generate practical boundaries and color ranges that were separate enough to differentiate between the obvious typical variances in conch pearl color, but would not be difficult to understand. They have done one quick illustrative experiment, where a piece of Queen conch shell was exposed to X-ray radiation under X-ray luminescence instrument. The left side of the shell's surface was shielded from the radiation, while the right side was exposed to X-rays. After 15 minutes of exposure, the apparent color of the shell turned from pink–to purplish, with reduced saturation Hue and saturation changes observed on a piece of Queen conch shell after 15 minutes' exposure to X-ray radiation. Author organization has developed a consistent in-house color classification system and color masters for conch pearls, resulting in a comprehensive yet straightforward method to evaluate conch pearl color.

The purpose of Kanjanachatree et al [13] research was to find ways to increase the overall production and value of cultured half-pearls. They set out to find out the optimal mollusc size and evaluate the rejection rate, the mortality rate of the seeded molluscs, and the color and feature of the cultured half-pearl, and particularly any changes in the quality of the color from month to month in the cultivation of Pteria penguin. They concluded that, the RGB color of the cultured half-pearls seems to be slightly affected by the month if a trouble-free linear regression is fitted to the data. The smaller mollusks produced better-quality cultured half-pearls and had a lower mortality and rejection rate. The RGB colors of the cultured half-pearls had larger amplitudes of color variation over the incubation period than the colors in the larger pearl mollusks. The phases of the sinusoidal changes in RBG colors of the half-pearls are not in-phase (synchronous), so the overall color of the pearls changes over the year. This has important consequences for color matching.

Cartier and Krzemnicki [14] investigated cultivation Steps and Gemmological Investigations of Golden South Sea Cultured Pearls. Their focus was on production of cultured golden pearls from Pinctada maxima and their gemological study. They determined the comparison between three different "golden" yellow cultured pearls; Pinctada maxima, Pinctada margaritifera, and Hyriopsis schlegeli, with raman and UV-VIS spectroscopy. They concluded that, untreated high-quality golden South Sea cultured pearls from the Pinctada maxima oyster are rare and highly valued in the international market. Due to complexity (both ecologically and technically) related to cultivating these pearls is a restrictive factor in contributing to the market in large quantities of such high quality cultured pearls.

Zhou et.al [15], showed cultured pearls treated by Ballerina's method could be identified by their look, Raman photoluminescence, UV-Vis-NIR reflectance spectra, and different UV fluorescence intensities studied with Diamond View imaging. Ballerina was invited to treat 12 Tahitian cultured pearls particularly for their study. Naturally colored pistachio cultured pearls were also determined, and the results were evaluated with their treated pearls. Other properties indicated that bleaching might not play a vital role in changing the color of these pearls. The procedures may involve sophisticated chemical and physical techniques that can revolve natural gray colors into firm pistachio colors.

Before years of 2015, many scientists contributed to pearl research. Snezana Agatonovic-Kustrin and David W. Morton [16] discussed and concluded that a UV-Visible spectrum of a pearl is a unique property and different pearls may show differences in their UV-Visible absorbance due to differences in nacre composition. The nacre, also known as mother-of-pearl (MOP), is a crystalline substance that creates the iridescent visual effect attributed to pearls. Nacre is intensely studied because its biologically controlled microstructure contributes to its remarkable strength [17, 18]. Nacre is a biomineral composed mostly (about 95%) of thin layers of irregular polygonal platelets of aragonite, a crystal form of calcium carbonate ($CaCO_3$) and even thinner layers (5%) of conchiolin (a scleroprotein), separated by elastic biopolymers (such as chitin and lustrin) [19]. Each layer of nacre is considered as being optically non-uniform. It also states that Quantitative measurements of crystal orientation, platelet size, and platelet stacking direction show that orientational ordering occurs not abruptly but gradually over a distance of 50 µm. Self-ordering of the mineral phase is fundamental in nacre formation. The iridescent appearance and quality of nacre have been attributed to light diffraction, both diffraction, and interference (interaction between waves), or interference alone. The thickness of the aragonite platelets is about 500 nm, which is comparable to the wavelength of visible light (400–800 nm), leading to absorptive and reflective effects on different wavelengths of light and resulting in different colors of light being reflected when observed at different viewing angles. Thus, the iridescence color of the pearl varies with changes in both the angle of incident light and the angle of observation. This is due to diffraction caused by the reflection grating structure of nacre [20].

Scarratt et al investigated that the cause of color of Pinctada maxima nacre is not fully understood [21], However, Karampelas et al correlated that it is not only linked to the presence of natural color pigments but also, due to optical effects such as reflection and refraction at the surface and within the sub-surface nacre layer. [22] It is however, most unlikely that the color of Pinctada maxima is related to the presence of polyenes, as characteristic Raman peaks for these color pigments at approx. 1135 cm^{-1} and 1530 cm^{-1} are absent in Pinctada maxima . This is very much in contrast to pearls from freshwater mussels (e.g. Hyriopsis schlegeli) and many other marine molluscs colored by polyenes. This is commonly tested in laboratories by a combination of UV-Vis-NIR reflectance, Raman spectroscopy, photoluminescence, and trace element analysis. These analysis provide complementary information about the nature of the coloration, and its authenticity is well documented in the literature.

Another observation was that the freshwater pearls and saltwater pearls differ in the type of luster. The difference is due to the type of mollusc used to produce the pearls and the thickness of the nacre [16]. In appearance, Freshwater pearls are noted for a softer luster, a glow that comes from deep within the pearl as they are composed essentially of 100% MOP. The colors of pearls are not merely due to the pigments that may be present in the pearl but also from the reflection and refraction of light [6], the nature of the material surrounding the nucleus [7], and the overall structure of the pearl. There are three main factors contribute to overall pearl color; light phenomena (especially interference of incident light), pigments contained in the conchiolin, and the organic matter formed in the clearance between the inner surface of the nacre and outer surface of the bead. Color characteristics also differ according to the mother oyster species. The phenomenon of iridescence that shows glittering of various colors in a pearl is due to the interference and diffraction of light interacting with the specific structure on the pearl's surface [22]. Iridescence is usually considered together with luster in pearl grading. Another color phenomenon is overtone or glow. An overtone color is a translucent color that may sometimes appear on a pearl together with its original (body) color [21]. However, it may alter the body color somewhat [7].

Summing up on the species and color of the pearl, different molluscs produce pearls of different colors. The color of a pearl is usually similar to the color of the shell nacre of the mollusc which produces it; this character is genetically controlled. This is very clearly shown by Pinctada margaritifera (black or steel grey), P. maxima (silvery white), abalones (green) and freshwater mussels (pink). However, in the case of P. fucata, the color of the pearls produced may be golden yellow, pink, white or cream, depending on slight differences in the site of nuclei implantation. The pearls produced in the ventral region of the gonad are white or golden, while those produced in the dorsal region of the gonad in proximity to the hepato-pancreas are usually grey or white. Flawless pearls of a regular form are frequently seen among the pearls developed in contact with internal organs, such as liver, abyssal gland and, intestine. Pearls produced close to the retractor muscle tend to be baroque in shape with irregular protrusions and with a distinct black coloration. The thickness of the epithelium of the graft tissue is also considered to be responsible for determining the quality of pearls. A thin graft (2–10 μm) usually produces pearls with a good surface, while thicker ones (>20 μm) tend to produce dull and badly colored pearls [2, 23, 24].

In 2007, the 6th European Conference on Mineralogy and Spectroscopy discussed the role of polyenes in the coloration of cultured fresh water pearls. This work aimed to establish the relationship between color and the nature of the pigment mixture in cultured freshwater pearls using non-destructive methods. This subject rise in importance as the demand for colored pearls has grown over the past three decades. Pearls are composites of calcium carbonate, chiefly aragonite, and organic material, deposited in concentric layers [22]. Before and early 90's, with the help of advanced spectroscopic instruments like Raman Spectroscopy Fengming et al, and Urmos et al, [7, 25] studied that Raman scattering is used to detect pigments in natural saltwater and cultured freshwater pearls. These pigments have been identified as carotenoids but after this, studies Karampelas et al. [22] have shown that the color of pearl is due to a mixture of short unsubstituted polyenes and not carotenoids [26]. They stated that the origin of the variety of body colors exhibited by South Sea Pearls is in part due to a newly recognized structure of the nacre, the edge-band structure, which gives rise to interference colors characteristic of its width. With the pearl oyster, Pinctada maxima, the colors include a range of silver tones, creams, yellows, and gold in various degrees of color saturation. We establish here that the primary body color of P. maxima pearls arises from the interference of light within the binding regions of the aragonite tiles. The tile faces terminate in a fissured nano-composite structure containing organic matrix within the margin of the aragonite tiles. This edge-band structure gives rise to an optical film formed of organic matrix in aragonite. The non-metallic whiter pearls are more commonly seen and can be accounted for by disorder of this structure leading to unsaturation of the color. They also stated that there may be a problem in the case of a sample, which contains polyacetylenic pigments before the treatment, and the treatment does not add a Raman peak. Their research team is working with UV-Vis-NIR spectroscopy in reflection and luminescence spectroscopy to find a solution to this problem, as well as to the identification of treated-color saltwater pearls.

Shen Elen in 2002 [27] showed a comparison study among the white and yellow nacre of the gold-lipped Pinctada maxima oyster shell and studied 65 yellow cultured pearls, both treated and natural color, produced from their mollusc. The yellow nacre of that shell has a characteristic absorption feature in the UV region between 330 and 385 nm; the color became saturated showed by the absorption feature. His study showed to identify criteria that can be used to separate treated from natural-color material. The report compared heat-treated yellow cultured pearls to natural shell nacre and natural-color yellow cultured pearls from the Pinctada maxima.

Regarding the color of the pearl which is genetically controlled is clearly shown by certain mollusc. Pinctada maxima have a nacre of silvery white and thus it produces pearls of almost the same color [28]. Pinctada margaritifera has a greenish black or steel grey color shell and it produces the same color, meaning black or steel grey pearl. In freshwater mussels, pink color pearl produces. But in the case of Pinctada Fucata, the color of pearls produced depends on slight differences in the site of nuclei implantation and it may be golden yellow, pink, white or cream. Now when the nuclei are slightly implanted or produced in the ventral region of the gonad, it is white or golden. If it is in dorsal region nearest to the hepato pancreas, then it is usually grayish or white. When pearls develop a contact with internal organs such as liver abyssal and intestine, then the pearls are flawless and are in a natural form. When the pearl is produced near the retractor muscle, then it is nearly irregularly shaped and also has a different black coloration. The colors displayed by a pearl are a consequence of the interaction between incident light and the structure of the pearl's nacre. Fine pearls are somewhat iridescent; for they not only reflect light - they break it up into different colors. On high-quality white round pearls, this may result in a very subtle and a pinkish overtone. High luster pearls may also display flashes of rainbow colors.

3. PURPOSE

In the present day scenario, there is hardly any scientific pearl testing laboratory in India that can analyze and determine the identity of different types of pearls. It also determines their nature of origin, as to natural, cultured, dyed pearls, irradiated pearls and imitation pearl by using non destructive methods. Therefore an attempt is made on all the above aspects by using one of spectroscopic method i.e. RAMAN spectroscopy. Laser Raman spectroscopy with its principle of scattering of light helps in identification of primary matrix, as the external features are same in all types of pearls except those of the imitation pearls. The technique is explained along with different types of colored pearls.

4. METHODOLOGY

Several environmental factors play a predominant role in determining the color and luster of the pearl nacre. Water depth is one of the most important factors, as quality pearls tend to be produced in waters below 10 m. Fouling, water boring problems and siltation are considerably less at depths of 10 m or more. The pearl culture grounds also play a significant role in determining the pearl quality. A repeated culture on the same ground is proven to affect the quality of pearls. Organic substances discharged by the pearl oysters and fouling organisms get deposited on the sea bottom and their build-up eventually affects the chemical and physical state of the water. Periodic removal of these deposits increases the production of pearls with desirable quality. During the final “make-up culture” period, pearl oysters are shifted to places of potential quality pearl yielding grounds.

Temperature controls the metabolic rate of the molluscs. Higher temperature leads to faster growth in oysters and a higher rate of nacre deposition. However, this affects the quality of pearls. Thinner laminar nacreous layers, which result from low temperature and pH, are desirable at least in the later phase of the culture period since the thinner mineral laminae in the upper layers of the pearl give a better luster to the pearls. The physiological state of the pearl oyster and the condition of the culture ground affects the growth of the oyster and the size as well as the color of the pearl.

It depends principally on differences in chemical composition of the seawater, as well as the kind and amount of plankton in the area where the pearl oysters are reared. The chief source of conchiolin is the nitrogenous substances of the plankton, which influences the color of pearls. Minerals and trace elements in the seawater are important, as these also influence the color of pearls. It has been found that the golden and cream colored pearls contain more copper and silver, while skin colored and pink colored pearls contain more sodium and zinc. The golden colored pearls have been found to contain more metallic elements than green pearls. The pearl color varies according to the number of porphyrins and metalloporphyrins present in them. Iron-bound peptide in the nacre favours the formation of yellow pearls. The organic substances deposited at the beginning of the pearl formation also would influence the color. Good quality blue pearls are of this origin. Searching the bibliography, one notes that only a few molluscs species are used for commercial cultivation. For saltwater cultured pearls (SWCP) these are the bivalves Pinctada margaritifera, commercially called Tahitian cultured pearls-, Pinctada fucata (martensii) -commercially called Akoya cultured pearls-, Pinctada maxima -commercially called South Sea cultured pearls-, Pteria stema, and more rarely the univalve Haliotis iris -commercially called rainbow abalone pearls. For freshwater pearls, the following bivalves are used for cultivation: Hyriopsis schlegelii (H. schlegelii) -commercially called Biwa cultured pearls-, Hyriopsis cumingii (H. cumingii) commercially called Chinese freshwater cultured pearls- and the hybrid Hyriopsis schlegeliixcumingii -commercially called Kasumigaura freshwater cultured pearls [2, 24, 29].

In the last 20 years, the gem market has seen an explosion of interest for colored pearls. Freshwater cultured pearls (FWCP) occur in four primary hues -white, grey, orange and purple. However various combinations of tone and saturation yield a broad range of color appearances. Over the last few years the demand for colored pearls has increased significantly, thus treated-color pearls have also entered the marketplace in large numbers. Pearl color treatments fall into two categories: color before drilling and color after drilling. The most common dye is silver salts (i.e. silver nitrate, silver chloride , others) that turn the color of the pearl darker. Iodine is also used to turn the color of the pearl into yellow [5, 30]. Various organic dyes are also used for pearl's color treatment, to obtain a variety of colors. Carotenoid pigment is used to dye the pearl into golden and black colors [31]. Dyes and chemicals typically are used after drilling, to facilitate their entry parallel to the nacre layers [5] but pre-drilling can also be used [32]. Nowadays there are other treatments used for pearls such as irradiation, i.e. after exposure to y-rays, the pearls turn grey, bluish grey, and black- [2, 7] and heat treatment, i.e. it turns the pearl's color yellowish – [5, 33]. Both of the treatments above may be performed pre and post drilling. The challenge for the gem and jewelry industry is to separate natural-color cultured pearls, of any color, from the treated ones.

The primary method used for detecting pearl color treatment is visual observation (at different magnifications, from unaided eye to microscope in reflective light). An unusual color concentration can be detected in the form of a colored layer (visible in the drill hole, if the pearl is drilled) or a color spot or streak visible on the surface [2, 4, 5, 34, 35]. These areas are often more porous (as indicated by a cloudy or milky appearance before treatment), which allows the dye or chemical to become concentrated [5]. The relatively saturated color at the surface of the nacre, which becomes lighter as one looked deeper into the drill hole, suggests that the pearls exhibiting this feature were color treated before drilling [30]. Had color treatment been applied after drilling, it most likely would appear to color the nacre uniformly within the drill hole, or to be concentrated at the conchiolin layer between the nucleus and the nacre [30, 32]. However, the undrilled pearls, especially in the absence of obvious visual features are much more difficult to identify [5]. Moreover, colored FWCPs do not present any luminescence under short-wave and long-wave UV radiation. This method is thus useless, except if the nacre is rich in any "suspicious" pigment which generally suppresses the luminescence.

4.1 Types of pearls selected for investigation

In the course of present work large numbers of pearls were observed under microscope having different sizes, shapes and color. Out of that 9 samples which were having similar weight and almost similar dimensions were taken up for the further investigation. Generally such assorted small numbers based on similar dimensions would help to determine the quality, genuinity and to fix market price for the pearl market trade. This also helped to conclude the result with least error as the specimens were exposed under various spectroscopic investigations. Marine water Natural pearl from trade and marine water cultured pearls grown in Central Marine Fisheries Research Institute (CMFRI) located at Tuticorin, Tamilnadu, India [36] pearls from freshwater Hyriopsis, irradiated, dyed pearls and imitation pearls were the categories chosen for this present work, those are shown in figure 1. Author developed the marine water cultured pearl at the CMFRI. We also used Marine water natural and fresh water cultured pearl, dyed, irradiated and imitation pearl (obtained from the trade source).

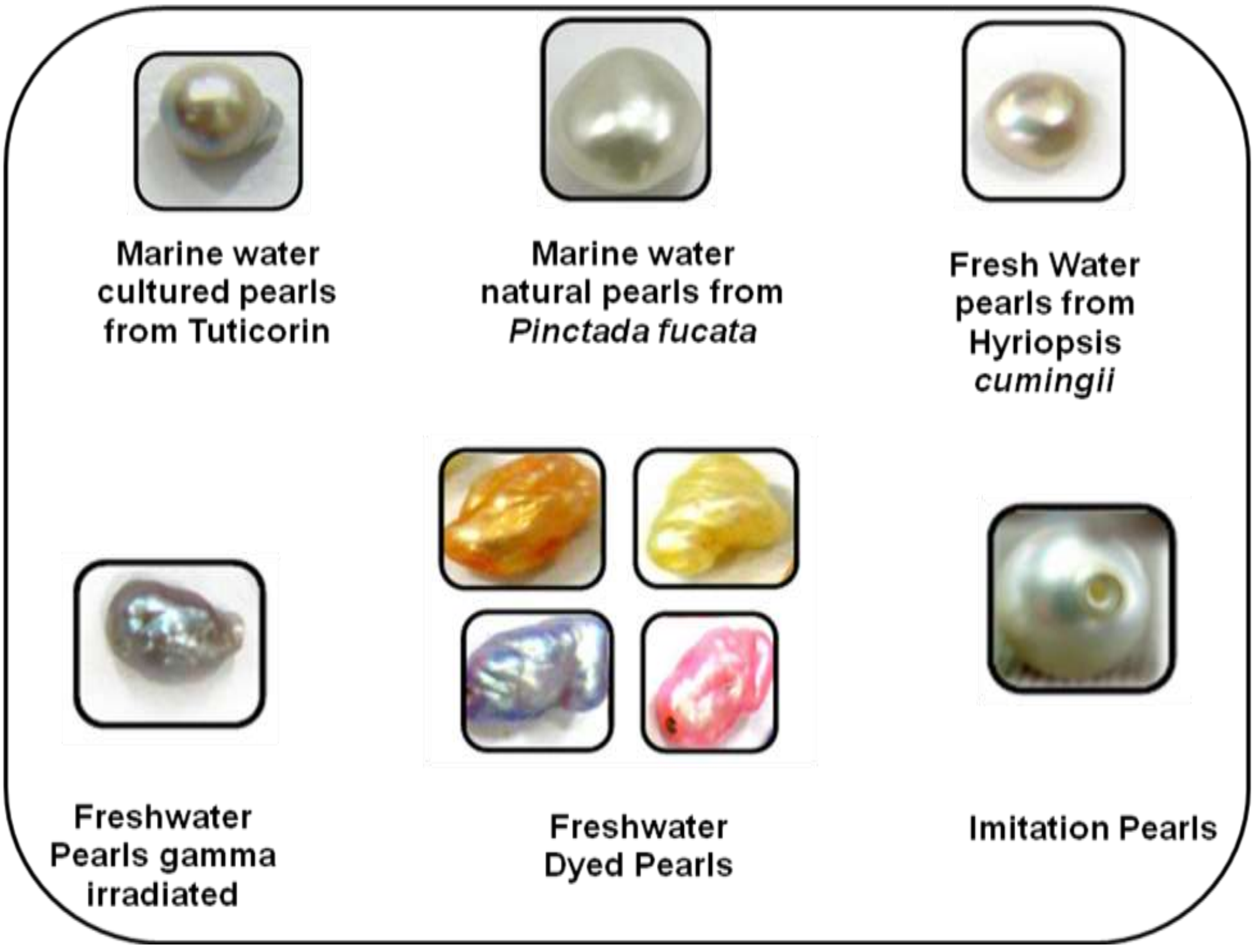

Fig 1: All pearl samples which were taken for investigation

4.2 Raman Spectroscopy and Photo Luminescence

4.2.1 Principle

When light falls on a substance in any phase i.e. gas, liquid or solid, it gets partly scattered and also can get absorbed under certain conditions. The absorbed portion of the light can be used to get information on the energy levels of electrons in the sample. This forms the subject matter of absorption spectroscopy. In the scattered portion of light most of the photons have the same energy as the incident light. This is "elastic scattering" which is named as Rayleigh scattering. When a small fraction of light (approximately 1 in 107 photons) is scattered at frequencies different from the frequency of incident photons, it is called as inelastic scattering. The process leading to this inelastic scattering was discovered by Sir C.V.Raman in 1928. The shift in the frequency of the scattered photon contains information about the vibrational/rotational/electronic energy of the scattering substance. Therefore the extent of frequency shift during Raman scattering gives information about the scattering substance. When intense monochromatic light falls on a substance at a microscopic level the electron cloud in the material interacts with time varying electric field associated with light quanta. In the case of inelastic scattering the electric field firstly distorts the electronic cloud and interacts with the electric dipole moment produced due to the distraction of the electronic cloud. The induced dipole moment depends on the polarizability of the molecule/medium. The induced moment also depends on the molecule/ lattice vibrations coupled to the electronic excitation. The vibrations exchange energy with incident photons are responsible for inelastic scattering of light (Raman Scattering). Hence Raman shift gives the vibrational spectrum of the substance. In the case of crystalline solids, it gives information about the structure. Hence Raman spectrum can be used as fingerprint in the identification of crystalline substances and its molecular constituents. With the advent of lasers which give intense monochromatic coherent light beam, Raman spectroscopy has evolved into a very powerful tool to quickly identify molecules in different substances and minerals. Raman scattering is a non resonant process. During the scattering process the molecule or crystal lattice is excited to a "virtual" state and when it gets deexcited if it ends up on any of the upper states (vibrational/rotational), the energy of the scattered photon gets shifted by an amount equal to that of vibrational energy of the molecule/solid [37, 38].

Photoluminescence gives information complementary to that observed in electronic absorption. Most of the electronic excitations are followed by the emission of light at longer wavelengths. This is called Photoluminescence (PL). PL measurements give information to chromophores and also other metallic impurities present in pearls. Experimentally Raman Spectrometer using 325 nm, 514 nm excitations can be used to obtain the PL spectra. Laser RAMAN spectra were obtained on Renishaw Laser-RAMAN spectrometer equipped with leica Microscope and facility to excite with two lasers 325 nm and 514 nm. Photoluminescence spectra also obtained from the same instrument.

5. RESULTS AND DISCUSSION

Raman Spectroscopy is a prerequisite for investigations of samples under test. Chemically the shell of pearls is made up of calcium carbonate CaCO3 in aragonitic phase. This is identified using Raman spectroscopy which gives the fundamental vibrations and spectra of calcium carbonate in this structural form. The spectra clearly agreed with those spectra reported in literature confirming the formation of pearls. The Raman Spectra is shown in figure 2 ,figure 3 and figure 4 for marine water natural pearl, marine water cultured pearl and fresh water cultured pearl respectively. It is clear that there is no difference in the results obtained for marine water natural pearl, marine water cultured pearl and freshwater cultured pearl. All three figures show the calcium carbonate peaks which indicates that the material under test is indeed a pearl and not imitation.

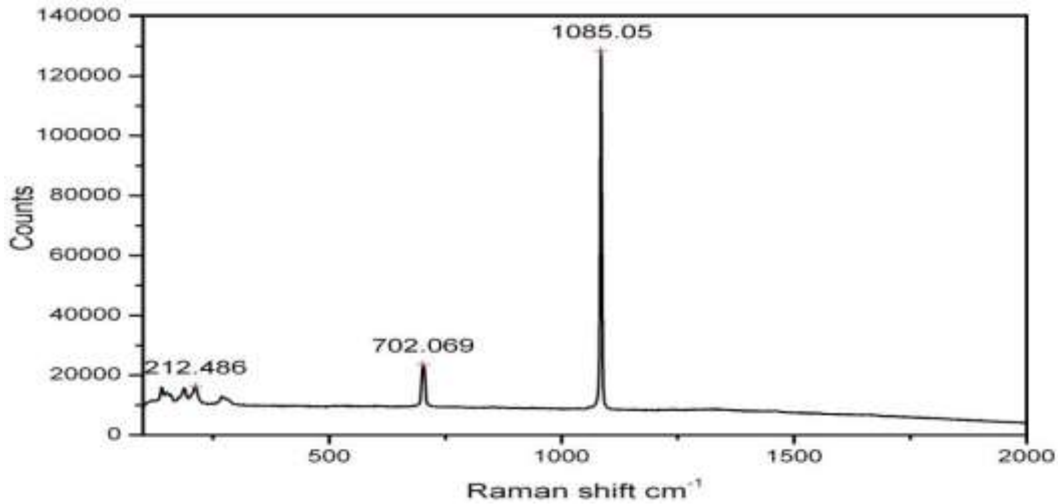

Fig 2: Laser Raman Spectra of Marine Water Natural Pearl

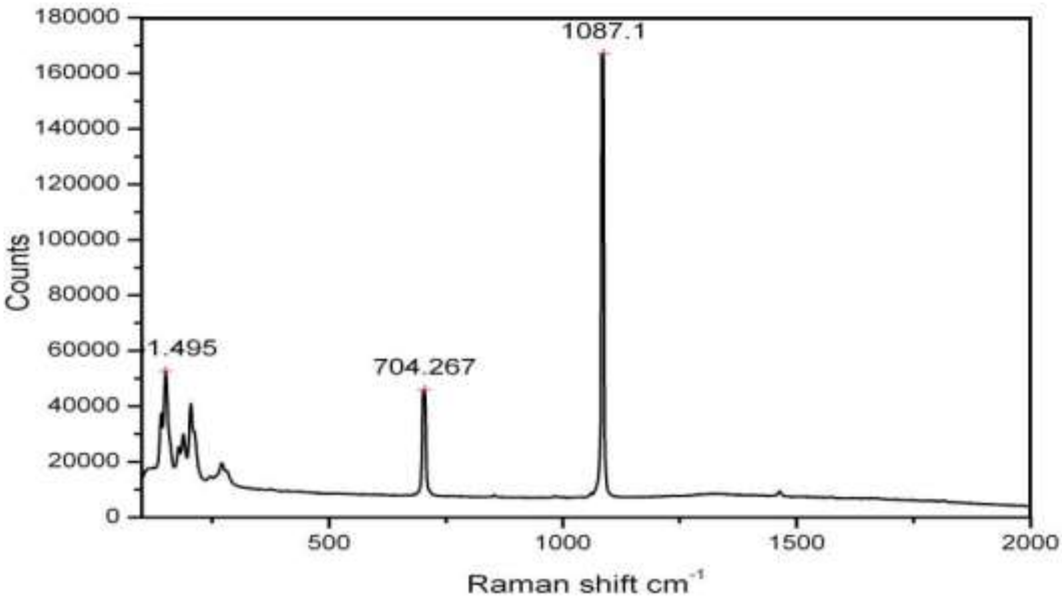

Fig 3: Laser Raman Spectra of Marine Water Cultured Pearl

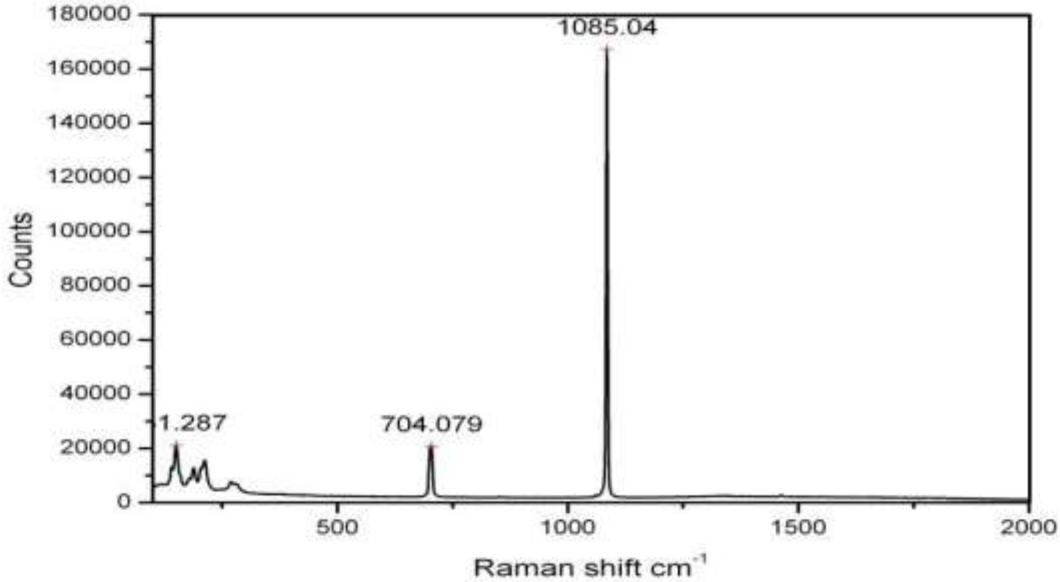

Fig 4: Laser Raman Spectra of Fresh Water Cultured Pearl

It is observed from the above analysis that in the case of imitation pearls, the calcium carbonate peak is also present along with other peaks characteristic for the impurities present in the imitation pearl (Figure 5). A visual comparison of the spectra obtained in figure 2, figure 3 and figure 4 shows that the spectra obtained for the imitation pearl is distinctly different from those obtained for natural, cultured and freshwater cultured pearl. Mainly the imitation pearl not only has the calcium carbonate peak at 1086cm^{-1} but it also has other peaks at 750cm^{-1}, 1340 cm^{-1} and 1542 cm^{-1} which indicates that the base material for the imitation pearl is a shell. The shell bead is coated with some pigments. The imitation pearl with a shell base revealed Raman spectra as shown in figure 5.

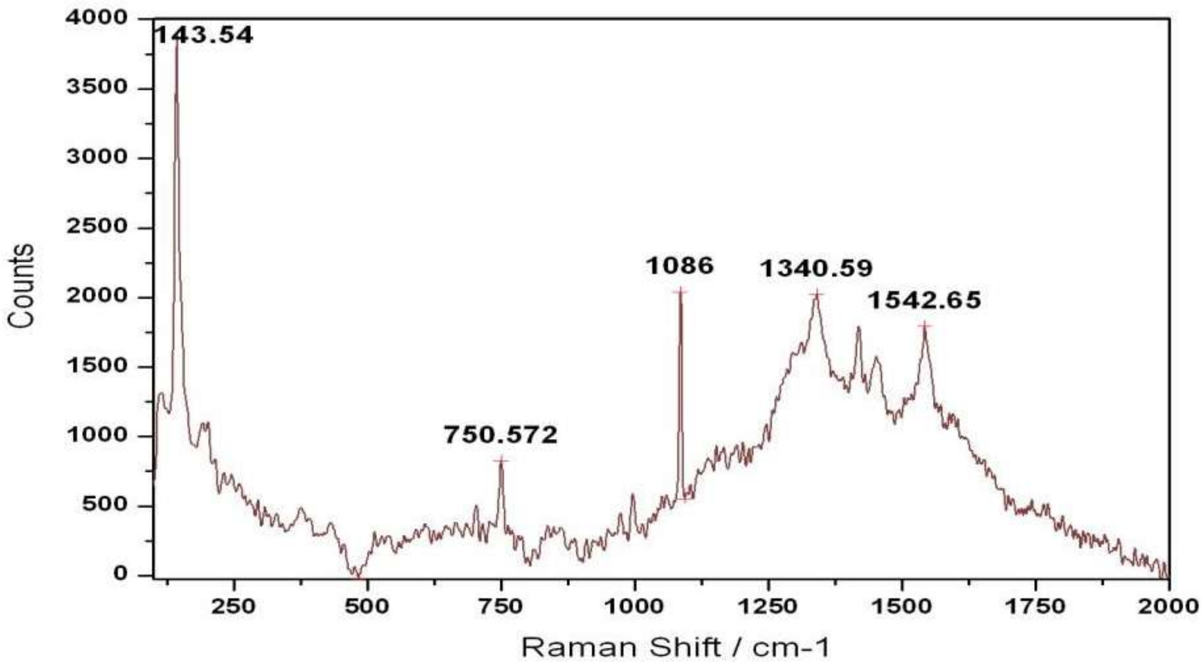

Fig 5: Laser Raman Spectra of Imitation Pearl

Bright pigmentation observed in naturally colored pearls and corals are known to arise from the presence of relatively few, widely distributed organic molecular species. Prominent among such colored substances are melanins, tetrapyroles, hydroxyl-naphto-quinones and fat-soluble lipochromic polyenes. Polyenes are polyunsaturated organic compounds that contain one or more sequences of alternating double and single carbon–carbon bonds (polyenic chain).

The vast majority of these pigments belong to the carotenoid family. Carotenoids can chemically be described as conjugated polyacetylenic molecules of finite length, having varied substitution on the terminal ends of a polyene chain, as well as the characteristic four methyl groups substituted on the polyenic backbone. It has been known that there are some pigments found in some parrot feathers e.g. Ara Macao and some coral species especially Corallium rubrum [39] which give specific color to the feathers and to the corals.

These pigments can be identified by Raman Spectroscopy as it is a uniquely suitable tool for the study of poly-conjugated molecules as they have delocalized-electrons. In the case of fresh water colored pearls one can also observe these peaks which are due to certain polyenic-chains. Two strong Raman resonant bands, due to polyenic chains, are observed in the ranges 1100–1200 and 1450–1600 cm^{-1} for the freshwater colored pearls (Figure 6A and B). These bands correspond respectively to the carbon–carbon stretching vibration of a C–C single bond (coupled to C–H in-plane bending modes), and to that of a C = C double bond in a polyenic- chain [40]. The exact position of these bands, however, depends on the number of C=C double bonds and length of the chain [41, 42].

This strong spectral enhancement is the coupling of electronic and vibrational transitions in polyenic chain result in Resonance Raman effect particularly when excited by 514 nm. This in turn results in highly enhanced intensity of Raman bands. Figure 6A and B shows the 514nm excited Raman spectra of four colored pearls along with that of a white pearl. All the colored pearls show intense 1131.7 cm^{-1} and 1522.5 cm^{-1} bands corresponding to C-C and C=C stretch of polyenic chains that incorporated during the natural growth of the pearl. These bands are absent in white pearl.

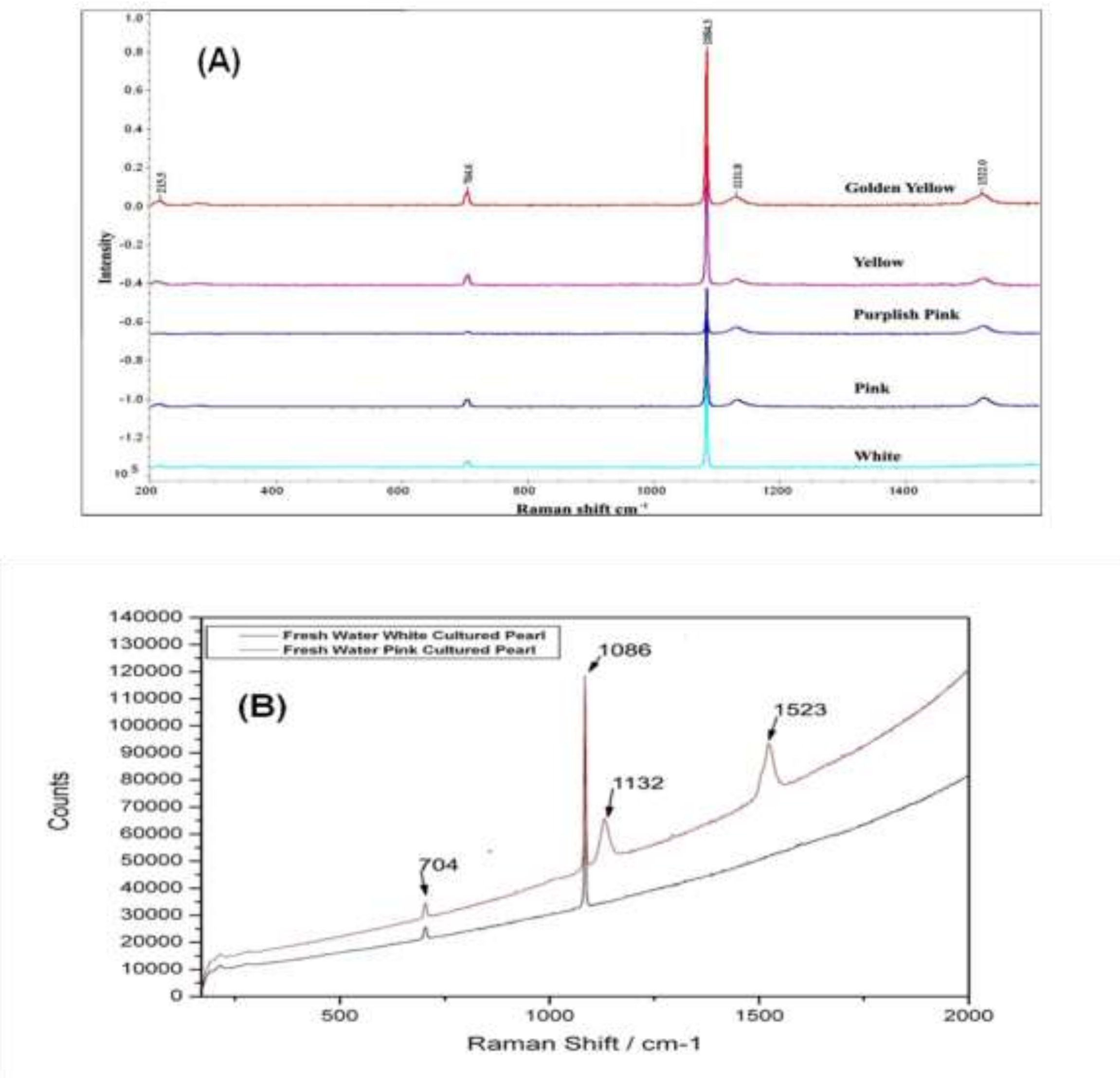

Fig 6 A & B: Raman spectra of colored freshwater cultured pearl

One can see that the freshwater pearls come in different shades of pink cream yellow. It is essential to know whether the coloration is natural or whether treatment has been done. From Raman spectra one can get a fair understanding of the fact that the above colors are of natural origin especially when one compares the Manganese (Mn) content in the pink calcite and in Marine pearls. The pink color is more due to the arrangement of the aragonite crystals and certain organic compounds elucidated further.

It may be seen clearly from the photoluminescence peaks obtained with 325 laser for the freshwater pearl and marine water pearl in figure 7. It shows that the 5% Mn containing natural pink calcite is present in the freshwater pearl which shows sharp peak at 341 nm followed by a shoulder at 372 nm, which are absent in other colored pearls. This clearly indicated that the pink color in pearls was not due to divalent Mn but due to a small concentration of polyenic chains in pearls.

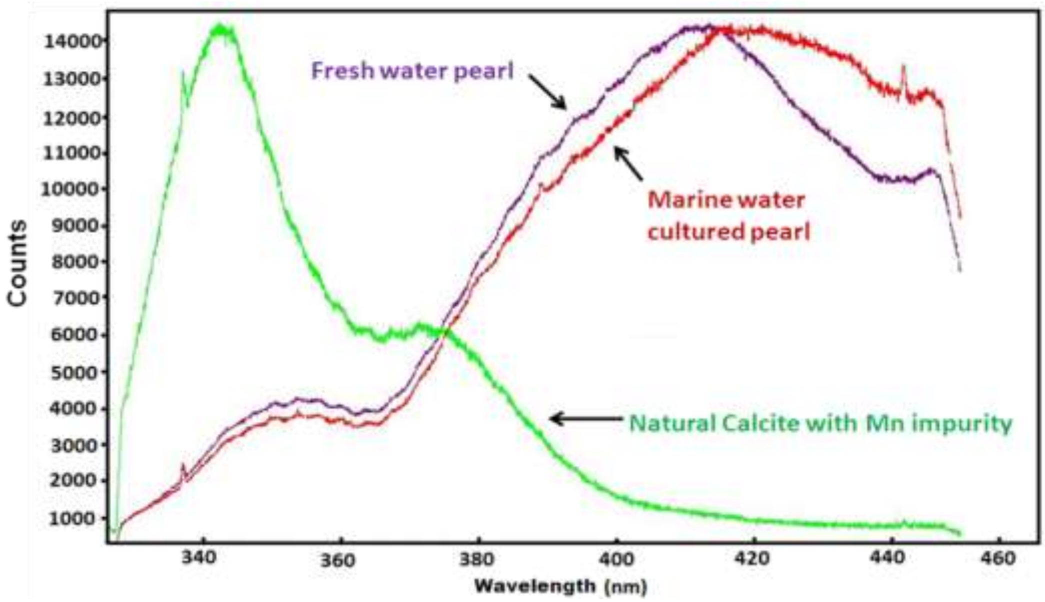

Fig 7: Photoluminescence of natural pink calcite, of freshwater pearl and marine water pearl

The occurrence of 1131.7cm^{-1} and 1522.5 cm^{-1} band in Laser Raman spectroscopic measurements was observed in Figure 6. It revealed that the pearls are not artificially colored and the origin of color is due to natural factors like the peak for pearl 1085 cm^{-1} was also present. Gamma irradiated fresh water pearls are grey in color and appear to look identical to some of the natural grey colored pearls. Irradiation is a process done on pearls to obtain grey color.

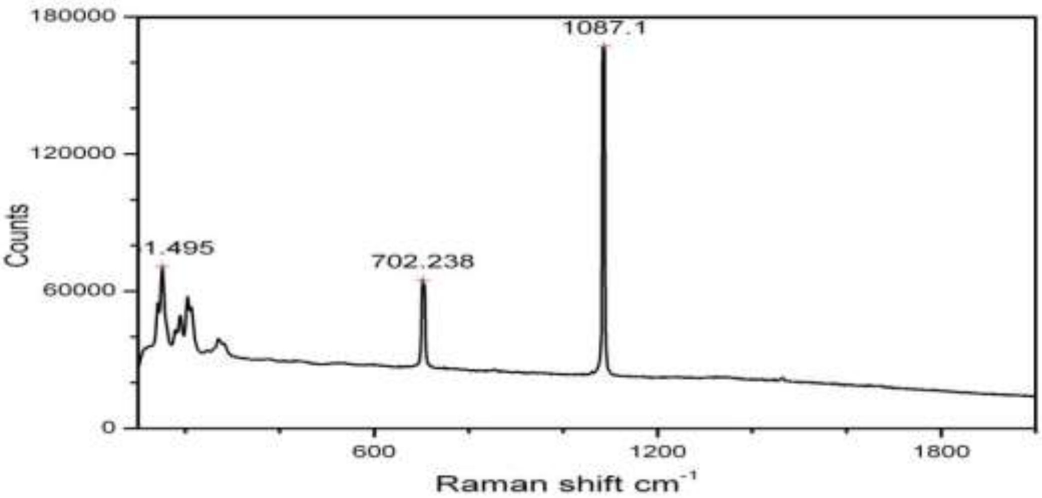

Fig 8: Raman spectra of Gamma irradiated Freshwater pearls

In the case of Gamma irradiated treated fresh water pearls one could be observe as in the Figure 8 that the 1085cm^{-1} was observed. However, the peaks 1131.7 cm^{-1} and 1522.5 cm^{-1} band were absent, clearly indicating that the grey color was artificial and not of natural origin. The natural-grey colored fresh water pearls colored due to some organic compounds was reflected in the peaks as seen in the figure 6 (A) observed for all colored freshwater pearls but these peaks were not reflected in Figure 8 indicating that the color was due to the effect of gamma rays on the conchiolin present in the pearls.

6. CONCLUSION

Raman scattering is used to detect natural pigments on pearls and in some cases to detect color treatments. All the pearls present the characteristic peaks of aragonite at 702 cm^{-1} and 1085 cm^{-1}. Colored FWCPs peaks at around 1130 cm^{-1} and 1530 cm^{-1} which are characteristic of polyenic pigments. Recent studies have been shown that FWCP's natural colors are due to a mixture of polyacetylenic pigments. The presence of polyenic pigments cannot identify the natural origin of color in an FWCP. This is because in some cases small polyenic bands can be detected in treated-color samples. This is probably because of a small quantity of these pigments before the color treatment. Similar weak signals due to polyenic pigments may also be identified in white colored FWCPs. This is because these pigments present strong resonant phenomena.

From the data obtained, we can observe that Raman Spectroscopy is invaluable in the study of pearls, their chromophores and to identify their growth in natural environment. Raman spectroscopy has been used to identify the pearls from their imitation. As per the results obtained in the present study it was shown that all types of pearls, natural marine water, cultured marine water, fresh water pearls, fresh water dyed pearls,irradiated fresh water pearls are made up of aragonite phase of $CaCO3$ and predominantly show the 1086 cm^{-1} peak. Whereas the imitation pearls having shell material as base show this peak along with other peaks like 750.57 cm^{-1},143.5 cm^{-1}, 1340 cm^{-1} and 1542 cm^{-1}. It may be for the first time that imitation pearls having shell bases have been investigated and studied. The data is of vital importance especially as more and more imitation pearls are making their appearance in the trade as well as the authentification of the nature of origin of color.

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