Study on Inspection Mechanism of Organic Gems Based on Laser Raman Spectroscopy

Li Shi [1], Hui Chi [2], Yong Yu [3], Wei Wang [4]

[1] Classification and Identification Department of Harbin Customs Technical Center, Harbin 150001, China

[2] Harbin Customs Technical Center, Harbin 150001, China

[3] Harbin Customs Technical Center, Harbin 150001, China

[4] Harbin Customs Technical Center, Harbin 150001, China

Abstract: Raman spectroscopy is a fast and nondestructive analysis and detection technology. Raman spectroscopy contains rich molecular structure information of substances. Based on the application status of Raman spectroscopy in the field of gemstones, this paper further explores its application technology in the qualitative identification of organic gemstones. In this paper, natural Longpai, Koba resin and rosin were tested based on laser Raman spectroscopy. The identification difficulties of high imitations of natural resins in Longpai are solved respectively. Therefore, the application of Raman spectroscopy to the identification and analysis of high imitations of organic gem amber and its natural resin has great advantages and convenience.

Keywords: Raman spectroscopy, Organic gemstones, Gemstone inspection

1. Introduction

Throughout the ages, the most beautiful and precious thing in the world is precious stones. They are often compared to the crystallization of sage wisdom and the essence of all things on earth. People often pin their symbols and hopes on gems to express their kind and beautiful wishes.

Organic gems refer to materials that are generated by natural organisms, partially or completely composed of organic substances, and can be used for jewelry and decorations. At present, the output of organic gemstones in the world is decreasing, especially the shortage of high-quality and high-grade organic gemstone raw materials. For this reason, many countries regard organic gemstones as more precious than gold, and even regard them as hard currency reserves. Since the founding of the People's Republic of China, China's organic gem industry has made great progress. With the deepening of reform and opening up, the improvement of people's material and cultural life, and the expansion of foreign exchanges, people's interest in organic gemstones has become increasingly strong. China is changing from an exporter of organic gemstones to a consumer of organic gemstones, and organic gemstones have entered the homes of ordinary people.

Laser Raman spectroscopy is an analytical method that uses laser as the light source, based on the inelastic scattering between photons and molecules and atoms of matter, and the number of Raman lines, the magnitude of displacement and the intensity of band caused by molecular vibration are different, so as to identify the functional groups in molecules. Every substance has a specific Raman spectrum, which is the "fingerprint" of its basic chemical composition and structure. Because jade has different molecular composition and crystal structure, its Raman spectrum characteristics are also different. By characterizing the sample to be measured, useful information can be obtained to achieve the purpose of determination and identification. Compared with other conventional gemstone identification techniques, this technique can not only detect the main components of jewelry and jade, but also capture the composition and structure information of trace impurities, inclusions and other substances in minerals. It is an important method for nondestructive identification of organic gemstones. Because this technique has basically no requirements for the state of the samples to be detected, and has the characteristics of non-contact, non-damage, etc., it is widely used in the detection and analysis of rare and valuable samples such as jewelry and jade, ancient cultural relics,

etc.

2. Application of Laser Raman Spectroscopy in Gem Identification

2.1. Traditional detection and analysis technology

The high value of jade makes it better to be nondestructive in the testing process. Therefore, most traditional testing methods use some conventional instruments to observe its physical characteristics with the naked eye. Here are some commonly used auxiliary instruments, as shown in Table 1.

Table 1 Conventional analytical instruments for gemstones.

Name	Detection characteristics	Limitations
Refractometer	Material refractive index	Material refractive index
Dichroic mirror	Polychromatic light	The sample needs to be colored and transparent
Ultraviolet fluorescent lamp	Fluorescence and phosphorescence	Visual observation, based on personal experience
Spectroscope	Absorption spectrum	Can't distinguish between natural and synthetic
Polarizer	Optical and axial properties of materials	Transparent or translucent

In the appraisal of gemstones, there are obvious limitations in identifying some imitations of rare natural gemstones with similar gemological characteristics such as color and refractive index, especially synthetic gemstones with clean interior and no obvious inclusions, and identifying some optimized gemstones, and other conventional nondestructive testing methods such as infrared spectrum analysis, gemstone microscope, refractometer and spectroscope. The application of Raman analysis in this field shows obvious advantages.

Traditional detection methods not only rely on these instruments, but also rely on many years' experience of experts or practitioners in gem industry to a great extent. In fact, the accuracy of such identification results is difficult to determine. For the same kind of gemstones, because of their high similarity in appearance and similar physical characteristics, it is difficult for even gemstone experts to make a distinction, which requires the help of relevant modern detection technology.

Researchers at home and abroad often use polarized light microscopy, Fourier infrared spectroscopy, X-ray diffraction and other methods to analyze gemstones, but all of them have strict requirements on the size, thickness, smooth polished surface and other conditions of the samples. Usually, it is necessary to pretreat the samples in order to obtain the relevant information of the mineral composition of gemstones, which has many limitations in the application of gemstone identification. However, Raman spectrum analysis basically has no requirement on the state of samples. Using photons as probes to quickly and accurately obtain the molecular structure information of gemstones is an important auxiliary means to identify and analyze the information of material category, inclusion characteristics, color origin, origin and so on.

2.2. Introduction to Raman Spectroscopy

Raman scattering is caused by inelastic collision between light and object surface. Elastic and inelastic collisions may occur when the incident monochromatic photons interact with the irradiated object molecules. When elastic collision occurs, the frequency of scattered light does not change, but the original incident direction is changed. This part of scattering is called Rayleigh scattering. In the

case of inelastic collision, the frequency of the scattered light changes, which is different from the initial frequency of the incident light. At the same time, the incident direction also changes. This scattering is called Raman scattering. This part of the scattering light intensity is only $10^{-6}-10^{-10}$ of the total scattering light intensity, which is called Raman scattering. Figure 1 shows the schematic diagram of Raman scattering.



Raman scattering
(scattering light and incident light have different frequencies)

Figure 1 Schematic Diagram of Raman Scattering

Raman spectroscopy is a kind of analytical technology to measure the molecular vibration spectrum inside materials. Compared with other modern analytical technologies, it has its own unique advantages: materials are cheap and easy to get, suitable for micro samples, non-destructive testing, rapid measurement, remote and online measurement, and has a good development prospect.

2.3. Raman Spectrum Testing System

The Raman spectrum testing system is mainly composed of three parts: external optical path probe system, spectrometer system and computer system. The fixed wavelength laser emitted by the laser converges into a spot with a very small diameter through the focusing system to irradiate the sample surface, causing the sample surface to generate Raman scattering. The Raman signal is collected through the collection end of the probe and converged to the spectrometer system by fiber conduction. The cooling CCD detector inside the spectrometer receives the Raman scattering light signal and converts the light signal into electrical signal, Then the electrical signals are transmitted to the computer system in a series of ways for subsequent data processing and analysis. In this section, a miniaturized Raman spectrum testing system is built, and its effective spectrum range is $250-2400cm^{-1}$. In this paper, a miniaturized 785nm semiconductor laser is selected. The maximum output power is 250mW, the spectral linewidth is<0.2nm, the spectral stability is<0.005nm/℃, and the operating temperature is 0 ℃ - 40 ℃.

2.4. Application of Raman Spectroscopy in the Detection of Organic Gems

In recent years, the application of laser Raman spectroscopy in the identification and analysis of organic gems such as pearls and amber has shown good results. Some scholars have further confirmed that the quality of pearls is obviously related to their crystal form through laser Raman spectrum analysis with different wavelengths. They used laser Raman spectroscopy to study the relationship between the color of high-quality freshwater pearls and their organic substances. The characteristics of laser Raman spectroscopy of high-quality freshwater cultured pearls with different colors are obviously different; With the deepening of the same color; The intensity of Raman peaks of organic compounds gradually increased. They compared and analyzed the Raman spectra of dyed black pearls, irradiated black pearls and Tahiti black pearls, and found that the Raman spectra of dyed black pearls had the characteristic Raman shifts of dyes. The irradiated black pearl has strong fluorescence and

only weak aragonite vibration peak can be seen. Raman spectrum of black pearl in Tahiti shows porphyrin peak of organic pigment, which can quickly distinguish three kinds of black pearls. They tested the Raman spectra of amber samples from Baltic Sea, Dominica and Myanmar respectively, and found that the Raman spectra of amber were mainly caused by the vibration of carbon chain skeleton. The Raman spectrum characteristics of amber from the same place are basically the same; Ambers from different habitats have little difference only in individual Raman shifts, and Raman spectrum plays a certain auxiliary role in identifying the authenticity and origin of amber.

3. Organic gem experiment part

Raman spectroscopy was used to detect the natural Longpai, Koba resin and rosin samples. This method is convenient and fast without sample preparation. The detection equipment is the Raman spectrum detection system constructed in the previous section.

The experimental results showed that copa resin did contain mushroom like substances. This is an important judgment basis for the Raman wave number dispersion diagram of Koba tree natural bowl racket, Koba resin, rosin and Ryu Po. After a large number of tests were carried out on more Longpai samples, it was found that some of the glass pai samples also had Raman vibration peaks similar to the Koba resin, but under the same test conditions, the peak intensity was significantly weaker than that of the Koba resin. The older the blubber is, the fewer the mushroom like substances in its components are, the less obvious the vibration peak lower than $1400cm^{-1}$, and the higher the polymerization degree of the polymer in Longpai is. Some Longpai samples will show strong fluorescent packets in the $200\text{-}1400\text{cm}^{-1}$ range, and the two vibration peaks at the $1400cm^{-1}$ and $1600cm^{-1}$ wave numbers will therefore become less obvious. The big difference between rosin and the other two is that there is a side peak of $1591cm^{-1}$ on the left side of $1625cm^{-1}$. Because the main component of rosin, resin acid, is unsaturated acid and has a conjugate double bond, the vibration peak at $1591cm^{-1}$ is the vibration peak of the conjugate double bond $C=C$. The other two substances do not have the conjugate double bond, so there is no vibration peak at this position. This is the spectral basis for distinguishing the characteristics of rosin and the other two.

The Raman spectra of the three are very different, and they do not cause any damage to the samples, so they are ideal spectral identification methods for organic gems. Finally, the detailed vibration study of the Raman spectrum of Coba resin shows that it does contain mushroom alkene compounds, which is the first time to provide strong evidence for it by Raman spectroscopy.

4. Conclusions

Aiming at the analysis and detection technology currently applied in the field of gemstones, the principle of Raman spectroscopy is introduced in detail and its advantages in the field of gemstones are pointed out. At the same time, the application status of Raman spectroscopy in this field is expounded. On this basis, the application technology of Raman spectroscopy in the field of qualitative identification and origin discrimination of gemstones is further explored. In this paper, the construction of Raman spectrum measurement system is realized. The miniaturized Raman probe realizes the miniaturization of the structure by integrating the laser with the external optical probe. Three kinds of organic gems, natural amber, rosin and Coba resin, were determined and distinguished by this system.

However, at present, laser Raman spectroscopy still has many limitations in nondestructive identification of jewelry and jade: when the sample has fluorescence, the fluorescence background of its Raman spectrum is easily disturbed, thus affecting the accuracy of the results; In addition, for some rare gems, because the information of spectral library is not perfect, it is impossible to obtain the results through information comparison. With the in-depth study of laser Raman technology and the gradual enrichment of Raman spectrum library, the application of laser Raman spectrum analysis in nondestructive identification of jewelry and jade is more in-depth and extensive.

References

[1] Li S, Ma W J, Yan R, et al. Temperature dependence of Raman spectra in single-walled carbon nanotube rings[J]. Applied Physics Letters, 2008, 92(12):121905.

[2] Bocklitz T, Walter A, Hartmann K, et al. How to pre-process Raman spectra for reliable and stable models?[J]. Analytica Chimica Acta, 2011, 704(1-2):47-56.

[3] Sahin H, Tongay S, Horzum S, et al. Anomalous Raman Spectra and Thickness Dependent Electronic properties of WSe2[J]. Physical Review B, 2013, 87(16):1106-1115.

[4] Park J S, Reina A, Saito R, et al. band Raman spectra of single, double and triple layer graphene[J]. Carbon, 2009, 47(5):1303-1310.

[5] Larouche N, Stansfield B L. Classifying nanostructured carbons using graphitic indices derived from Raman spectra[J]. Carbon, 2010, 48(3):620-629.

[6] Auer B M, Skinner J L. IR and Raman spectra of liquid water: Theory and interpretation[J]. Journal of Chemical Physics, 2008, 128(22):2210.

[7] Roehrl J, Hundhausen M, Emtsev K V, et al. Raman spectra of epitaxial graphene on SiC(0001)[J]. Applied Physics Letters, 2008, 92(20):666.

[8] Batista A J, Vianna P G, Ribeiro H B, et al. QR code micro-certified gemstones: femtosecond writing and Raman characterization in Diamond, Ruby and Sapphire[J]. Scientific Reports, 2019, 9(1):8927.

[9] Chen, Liang, Don, et al. Using Raman Spectroscopy for Gemstone Analysis[J]. American laboratory, 2017, 49(5):32-34.

[10] Thomas S M, Thomas R, Davidson P, et al. Application of Raman spectroscopy to quantify trace water concentrations in glasses and garnets[J]. American Mineralogist, 2008, 93(10):1550-1557.