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Raman Spectroscopy & µ-XRF

Spectroscopic Analysis Explains the Mystery of Dragonfly Eye Beads

Application Note

Multitechniques
RA-XRF-02

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Abstract: Spectroscopic analysis can reveal the origin of cultural heritages and the historical background at the time. This application note introduces research of a dragonfly eye bead found in a tomb in China. Using Raman spectroscopy and X-ray analytical microscopy, the bead was found to be from the Eastern Mediterranean region and the result suggested China had cultural and economic exchanges with them during that era.

Keywords: Archeology, Dragonfly eye beads, Raman spectroscopy, X-ray analytical microscopy (µ-XRF)

Introduction

Dragonfly eye beads are a kind of glass ornaments with an eye pattern, which were produced in Egypt first and introduced to China from the late Spring and Autumn period to the early Warring States period.[1,2] They were familiar among the princes and nobles in the period. Due to the high demand from the nobility, Chinese artisans began to copy the dragonfly eye beads that originated from Eastern Mediterranean region, which directly increased the local market and production of the glass. Research of these dragonfly eye beads can provide important insights into the cultural and economic exchanges between China and other countries during the period as well as the origin of the beads in China.

Chemical composition analysis, phase analysis, and element analysis are important for material science, as well as for archeology. XRD is an analytical technique for phase identification. It is generally difficult to analyze the micro-area of the sample due to the large spot size. SEM-EDX is an elemental analytical technique with micro-spot, but it cannot distinguish the colors of a sample visually. Moreover, it sometimes requires coating treatment such as carbon or gold coating, but the sample treatment is not suitable for precious cultural heritage. Raman spectroscopy and X-ray analytical microscopy are beneficial to analyze precious cultural heritage because of their advantages of micro-spot, non-invasion, less sample pretreatment, and high speed detection. The combination of the two techniques can cover all the above analysis categories.

This application note introduces research of a dragonfly eye bead using the XploRA confocal Raman microscope and the XGT-9000 X-ray analytical microscope.

Sample Information

Figure 1 shows a group of dragonfly eye beads unearthed from the tomb of Chu who was a Chinese nobleman during the early Warring States period. The tomb is located in Xujialing, Xichuan, Henan Province, China. Figure 2 shows one of the dragonfly eye beads from the tomb. The dragonfly eye bead was analyzed in this application note.

Figure 1. A series of dragonfly eye beads unearthed from the tomb of Chu, a Chinese nobleman during the early Warring States period.

Figure 2. A dragonfly eye bead analyzed in this application note. The red line shows the area of interest in this research.

Composition Analysis of a Dragonfly Eye Bead

First of all, chemical composition analysis and phase analysis were conducted on the dragonfly eyeball in Figure 2 using the XploRA confocal Raman microscope (Figure 3). Figure 4 shows the Raman spectra of the blue matrix area, the dark blue eyeball area, and the brown eye ring area of the sample. The result shows there are two specific envelopes in all the spectrum. One is the Si-O stretching envelope (i.e.,~1000 cm^{-1}) and the other is the Si-O bending envelope (~500 cm^{-1}). The result suggested that the dragonfly eye bead was made of glassy material.

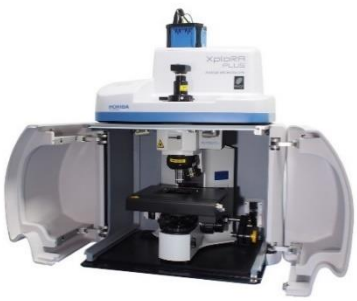

Figure 3. XploRA confocal Raman microscope.

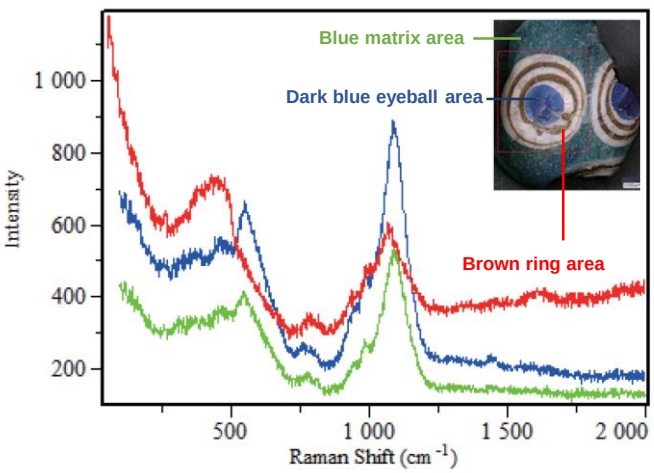

Figure 4. Raman spectra on the dark blue eyeball area, the blue matrix, and the brown ring area of the dragonfly eye bead acquired with the XploRA.

Next, to know the elemental composition of this bead, point analysis was performed using the XGT-9000 X-ray analytical microscope (Figure 5) on the target area within the red line of the sample. Table 1 shows the elemental composition of the sample. It is the average composition of the area within the red line. The quantitative result is calculated in the form of oxide. It revealed that the sample was made from glass mainly consisting of 70.56% of SiO_2, 9.78% of Na_2O, 9.29% of CaO, and less than 1% of MgO and K_2O. This trend indicates that the glass was a natron-type soda-lime-silicate (Na_2O-CaO-SiO_2) glass which was a typical type of glass made in the ancient Eastern Mediterranean region.

To investigate the elemental distribution, elemental map imaging was carried out on the area within the red line of the sample. Figure 6 shows the elemental distributions acquired with the XGT-9000. The result shows that different color areas consist of different elements. Ca and Sb were detected in the white ring areas, as well as K. The unclear boundary of Sb distribution suggested that Sb osmosed into the brown ring areas and the dark blue area. Co and Fe were detected in the dark blue eyeball area. Fe was also detected in the brown ring areas, as well as Mn. Cu was detected in both two types of blue color area.

Figure 5. XGT-9000 X-ray analytical microscope.

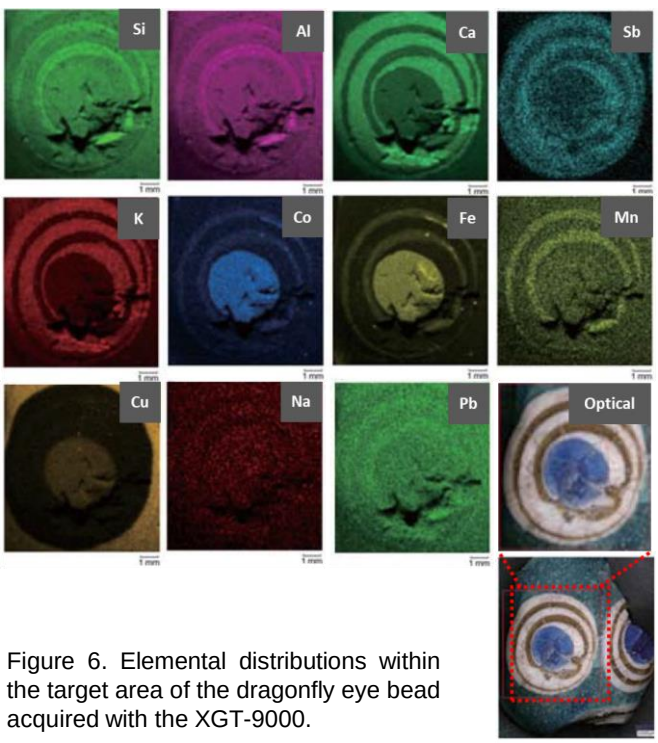

Figure 6. Elemental distributions within the target area of the dragonfly eye bead acquired with the XGT-9000.

Table 1. The average composition (wt%) of the target area of a dragonfly eye bead acquired with the XGT-9000.

Na_2O	MgO	Al_2O_3	SiO_2	Cl	K_2O	CaO	Fe_2O_3	CoO	CuO	Sb_2O_3	Mn_2O_3	SO_3	SrO	BaO
9.78	0.63	4.14	70.56	0.45	0.84	9.29	0.79	0.01	0.28	2.67	0.03	0.46	0.03	0.03

Exploring the Coloring Technique of the Bead

To investigate the colorants used in the dragonfly eye bead, point analysis was performed on each color area (white, dark blue, blue, and brown) of the sample using the XGT-9000. Table 2 shows the elemental quantification results of the color areas. Based on the values in Table 2, Figure 7 visualizes the trend of the contents of Ca, Sb, Fe, Cu, Co, and Mn on each color area. The results show that the white area has higher concentrations of Ca and Sb among the color areas. The brown circle area has higher concentration of Mn, which can be considered as the chromophore responsible for the brown color.[3] The dark blue area has higher concentration of Fe and Co. Co^{2+} is known to have a strong coloring effect to give a dark blue color even if with a concentration of a few tenths of one percent.[4] The result of the dark blue area was consistent with this. The blue matrix area has higher concentration of Cu than other areas. Cu^{2+} is known to make glass blue.

Table 2. Elemental quantification results (wt%) of the different color areas on the dragonfly eye bead acquired with the XGT-9000.

Color	Na	Mg	Al	Si	K	Ca	Fe	Sb	Cu	Co
white	13.59	0.21	0.00	58.17	0.00	16.78	0.71	9.14	0.02	0.00
dark blue	13.09	0.36	0.00	61.04	1.59	13.38	3.86	4.18	0.75	0.23
blue	8.75	0.00	0.38	66.98	3.36	13.58	0.76	0.99	2.52	0.00
brown	22.16	0.00	1.11	55.40	2.23	10.51	1.51	5.04	0.03	0.00

Color	Mn	Ti	Sn	Sr	S	Pb	Zn	Cl	Ba
white	0.04	0.00	0.14	0.09	0.38	0.07	0.00	0.00	0.66
dark blue	0.00	0.12	0.24	0.09	0.33	0.04	0.14	0.00	0.55
blue	0.00	0.10	0.51	0.10	0.40	0.16	0.00	1.16	0.26
brown	0.11	0.24	0.12	0.07	0.37	0.00	0.04	1.04	0.00

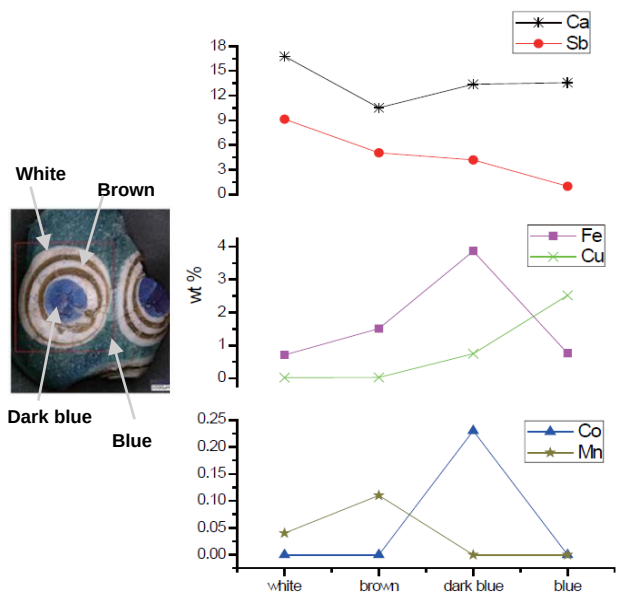

Figure 7. The trends of the elemental compositions (wt%) on each color area of the dragonfly eye bead.

To identify the chemical structure of the colorants, point analysis using the XploRA was performed on the white area and the dark blue area of the bead. Figure 8 (a) shows Raman spectrum acquired on the white ring area. The Raman bands found in Figure 8 (a) were consistent with the previous research reporting of the characteristic Raman bands of calcium antimonate ($CaSb_2O_6$) crystalline.[1,5] The $CaSb_2O_6$ was not used as an opacifier or white colorant for glass materials in China in the period. It was known to be generally used in ancient Egypt and other Eastern Mediterranean countries.[6] Figure 8 (b) shows a Raman spectrum on the dark blue eyeball area. A Raman band of $CaSb_2O_6$ around 669 cm^{-1} was also detected in Figure 8 (b), but it is overlapped with the Si-O bending envelope. This is consistent with the result in Table 2 showing the detection of Sb and Ca in the dark blue area. It indicates the osmosis from the white area into the dark blue eyeball area happened during the glass making process in which the hot white frit was inlaid into the material around it.

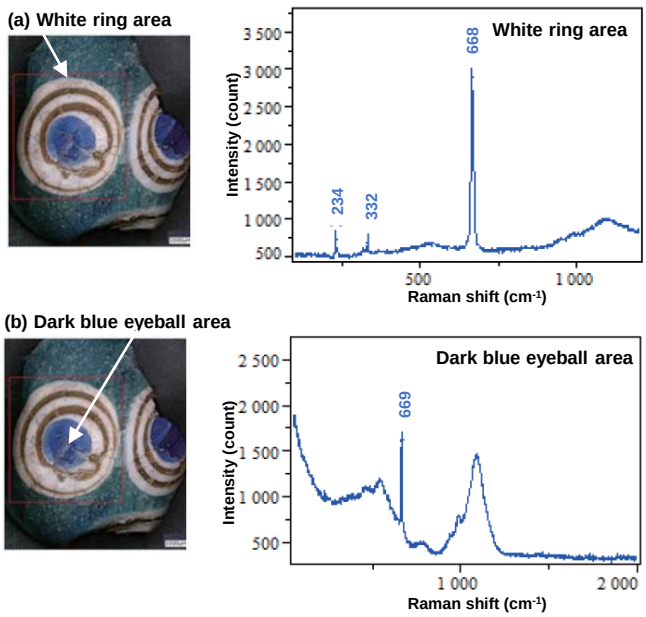

Figure 8. Raman spectra acquired with the XploRA (a) in the white ring area and (b) in the dark blue eyeball are of the dragonfly eye bead.

Conclusion

The chemical composition analysis and the phase analysis with the XploRA and the elemental analysis with the XGT-9000 are complementary for each other. The both two techniques revealed that the dragonfly eye bead in this application note was a typical soda-lime glass and used typical coloring technique used in the ancient Eastern Mediterranean countries. It played important roles not only of investigating the origin of the dragonfly eye bead found in China, but also of indicating the cultural and economic exchanges between China and other countries during that era.

Acknowledgement

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