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Analysis of the Characteristics of Celadon Raw Materials Based on EDXRF

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To discover the impact of different size of beam spots on the characteristics and main components of celadon raw materials in EDXRF and to further understand the uniform characteristics of the glazing color of different celadon products on this basis. In this paper, the characteristics of raw materials of different celadon products are tested under two conditions, namely with the beam spot diameter of 2 mm and 100 μm respectively. The test results of different conditions show that under different beam spot conditions, the stability of test data of celadon products is different. The test data of large beam spots are relatively stable and with good reproducibility while the variation of data under micro beam spot conditions is relatively significant. It can be seen from this study that the micro-zone analysis based on the EDXRF can improve the analysis accuracy of the characteristics of ancient ceramic raw materials.

1. Introduction

At the present stage, with the continuous development of porcelain manufacturing technology, the method of studying ceramic utensils from the perspective of elemental composition has been relatively mature and the nondestructive testing analysis of elemental composition has been widely used. EDXRF, as one of the important methods for the non-destructive testing of ancient ceramics, has also been widely used at this stage with the development of scientific detection instruments and technologies. The X ray beam diameter of the EDXRF Fenix method is increasingly smaller and the beam diameter can reach 40μm or even less. Therefore, the development and improvement of this technology also provide more possibilities for the micro probe analysis of ancient ceramics. Normally, the beam diameter used in the study of the characteristics of ancient ceramics is only a few millimeters. With the development of science and technology, the beam diameter has changed. Different beam diameters have a great impact on the test results and there is no specific study on whether this difference will have a qualitative impact on ceramic products of different ages and from different producing areas.

Based on this, this paper selects celadon of different ages and from different producing areas and uses modern analytical instruments to analyze and compare the celadon enamel composition under conventional beams and micro-beams. On the one hand, the technological characteristics of celadon products are analyzed from the perspective of homogeneity, and on the other hand, the difference of detection results of celadon products under different beam conditions is analyzed, which provides some references for improving the analysis accuracy of ancient ceramics.

2. Literature review

Porcelain is a great invention of China, and Jingdezhen, the "millennium porcelain capital," is an outstanding representative of this country of porcelain. Wu et al. pointed out in the study that based on current archaeological findings, the Five Dynasties (AD 907-960) period was the start stage of Jingdezhen porcelain industry. At that time, Jingdezhen Porcelain had begun to take shape, and its kiln sites were mainly distributed on the banks of the South River and the current urban areas, such as Xiang Lake, Shengmei Pavilion, Sanbao Peng, Huangnitou, Luomaqiao and Shibadu. From the unearthed objects, it can be concluded that the varieties produced in the kiln mainly include daily-use ceramics such as bowls, plates, dishes, pots, etc.,

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mostly celadon and white porcelain (Wu et al., 2014). Wu's research stated that blue and white porcelain can be considered as one of the most influential and most successful ceramics in the history of Chinese ceramics development. It is painted on a blank material with a cobalt material, and after the glaze is fired, it shows a blue-colored underglaze colored porcelain, which has the effect of Chinese traditional ink painting. It can be said that since its birth, the blue and white porcelain had a close connection with the export. Once it appeared, it in turn promoted further exchanges between the Chinese and foreign economies, technologies and cultures, especially after Zheng He's move to the West (Wu et al., 2014). A large number of blue-and-white porcelains are exported, almost all over Asia, Africa, Europe and the United States. Their unique charm is cherished by the world. Li et al. performed experiments on the composition of porcelain tires, and they found that the composition of celadon and white porcelain tires has greater commonalities, such as the chlorine dioxide content of 15% to 23%, and the content of sulfur dioxide is basically higher than 70. %, with the typical characteristics of ancient "high-silicon low-aluminum" in southern China. In addition, the water content in porcelain body is about 3%, and the content of Cao and Mgo is low (Li et al., 2014). In the study, He et al. pointed out that according to the past research results of ceramics in Jingdezhen during the Song, Yuan, Ming, and Qing periods, the academic community generally believed that the Jingdezhen porcelain industry used the dual formulation of porcelain stone and kaolin from the Yuan Dynasty to make mother mould. Before the Yuan Dynasty, all the porcelains were made of porcelain and one-piece formulas. However, this view lacks research evidence of porcelain from the Five Dynasties period (He et al., 2015). Zhang et al. conducted an experimental study on the composition of celadon and white porcelain in Jingdezhen, the results showed that the white porcelain and celadon enamel of Xianghu kiln in the period of five generations of Jingdezhen were all CAO-based fluxes and belonged to high-temperature calcium glaze. Judging from the compositional features of enamel, the five-generation period of Jingdezhen white porcelain and porcelain porcelain glaze has begun to use the prescription of glaze stone and glaze ash. The content of CAO in the celadon glaze is obviously higher than that of the white porcelain glaze, indicating that the amount of glaze ash in the celadon enamel formulation is higher than that of the white porcelain enamel (Zhang et al., 2017). Li et al.'s research illustrated that the method of studying ceramics from the elemental composition at this stage has matured, especially the non-destructive testing analysis of the ceramic elements is widely used. The establishment of a large number of databases has enabled experts and scholars to determine the age, origin, and authenticity of pottery to a certain extent through the characteristics of ceramic elements (Li et al., 2017). Gong wrote in his research that as the main method for non-destructive testing of ancient ceramics, that is, energy dispersive X-ray fluorescence spectroscopy (EDXRF) analysis method, the current development of instrument technology is very rapid. The smaller the X-ray beam, the smaller the beam diameter is 40 μm or even lower, thus making the analysis of ancient ceramic micro-zones possible. In the past, the beam size usually used was about a few millimeters (Gong, 2014). Hou et al. performed a comparative experiment on the chemical composition of celadon. The results showed that under the condition of a beam spot diameter of 2 mm, the results of the measurement points of the same sample were relatively close. The factor load map showed that Huzhou original celadon, Yueyao celadon and Longquan celadon were distributed in three different regions, and even the same celadon was different due to the different kiln sites; however, under the conditions of beam spot diameter of 100 μm, the measurement point data of the same sample is significantly different, and the data of the factor load diagram of the sample is mixed into a cluster, which affects the correct judgment of the porcelain age, origin, and authenticity (Hou et al., 2017).

In summary, the development of China's porcelain, celadon, white porcelain, and the chemical composition of celadon in different regions are mainly compared and analyzed, and these aspects are specifically elaborated to understand the influence of different beam spots on the characteristics and main components of EDXRF celadon raw materials, and to further understand the uniform characteristics of the coating color of different celadon products. The celadons of different origins are selected, and modern analysis instruments are used to analyze and compare the celadon glaze compositions under traditional beams and microbeams. On the one hand, the process characteristics of celadon products are analyzed from the point of view of homogeneity. On the other hand, the differences in celadon product test results under different beam conditions are analyzed, which provides a reference for improving the analysis accuracy of ancient ceramics.

3. Experimental materials and methods of the characteristics of celadon raw materials based on EDXRF

3.1 Sample source

A total of 12 celadon samples are selected for this experiment, including 2 blocks of original celadon from Huzhou, No. Y1 and Y2; 5 blocks of celadon samples from Yue Kiln, No. P24, H1, JS3, YC6 and YD6; 5

blocks of celadon samples from Longquan kiln, No. HM15, LD7, ST15, ST17 and SW15. The celadon samples selected above have small curvature and are relatively flat.

3.2 Instruments and detection conditions

The instrument used in this test is the EAGLE-111 XXL large specimen chamber micro focusing X-ray EDXRF from EDAX Company in the USA. The rhodium target and Si detector are used for the X-ray tube. The maximum voltage of the tube is 50KV and the maximum current is 1000μA.
Two different test conditions are used in this study, as is shown in Table 1:

Table 1: Two different measurement conditions

Numbering	Beam diameter	Light tube voltage	Current	Resolution	Measure time	Light path type
1	2mm	15kv	150μA	145.4eV	300s	Vacuum
2	100μm	35kv	920μA	143.6eV	300s	Vacuum

4. Sample test and results

The surface of the sample glaze is first subjected to a cleaning treatment and the test is performed on the surface where the surface is smooth, flat and free of other particles. Five different spots are selected for each sample and the test results are shown in the following table 2, table 3, table 4, table 5:

Table 2: Huzhou original celadon enamel main chemical composition (2mm)

Sample	Na_2O	MgO	AL_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
Y1-1	0.66	1.52	17.57	70.72	0.62	2.84	3.41	0.33	0.07	2.26
Y1-2	0.50	1.21	18.75	70.31	0.50	2.72	2.50	0.32	0.07	3.11
Y1-3	0.50	1.26	18.23	71.31	0.54	2.87	2.65	0.33	0.06	2.25
Y1-4	0.46	1.21	20.46	69.70	0.44	2.90	2.04	0.33	0.05	2.40
Y1-5	0.42	1.17	19.39	70.02	0.55	2.99	2.73	0.33	0.05	2.35
Y2-1	0.65	1.43	16.84	67.78	0.69	2.46	6.70	0.36	0.10	3.10
Y2-2	0.62	1.35	16.91	68.81	0.67	2.48	5.93	0.36	0.09	2.78
Y2-3	0.63	1.29	17.36	67.78	0.60	2.80	4.73	0.38	0.09	4.34
Y2-4	0.60	1.45	16.33	67.75	0.77	2.50	7.24	0.38	0.13	2.83
Y2-5	0.65	1.69	15.02	60.83	1.18	1.74	15.90	0.34	0.12	2.53

Table 3: Yue kiln original celadon enamel main chemical composition (2mm)

Sample	Na_2O	MgO	AL_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
P24-1	0.54	1.63	11.66	60.40	2.30	1.95	18.43	0.22	0.80	2.07
P24-2	0.49	1.56	11.60	59.22	2.38	1.80	19.96	0.21	0.83	1.96
P24-3	0.52	1.62	11.54	59.22	2.42	1.85	19.90	0.21	0.83	1.90
P24-4	0.47	1.57	11.53	59.45	2.39	1.83	19.82	0.22	0.80	1.89
P24-5	0.47	1.58	11.65	59.65	2.40	1.86	19.37	0.21	0.68	1.94
H1-1	0.29	1.39	12.01	66.86	1.66	1.67	13.00	0.23	0.60	2.20
H1-2	0.31	1.40	12.49	67.91	1.63	1.83	11.38	0.24	0.69	2.22
H1-3	0.29	1.34	11.91	66.64	1.58	1.66	13.52	0.23	0.67	2.14
H1-4	0.34	1.38	12.24	67.29	1.65	1.73	12.33	0.25	0.66	2.12
H1-5	0.33	1.38	12.31	67.65	1.66	1.78	11.76	0.24	0.69	2.22

The above three tables are the main chemical composition of enamel obtained under the conditions of 2mm. in the following, the Huzhou celadon will be taken as an example to analyze the chemical composition obtained under the beam spot diameter of 100μm:

Table 4: Longquan celadon porcelain sample main chemical composition (2mm)

Sample	Na_2O	MgO	AL_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
HM15-1	0.22	0.66	13.51	70.65	0.20	4.58	8.38	0.04	0.13	1.63
HM15-2	0.24	0.62	13.82	70.17	0.20	4.45	8.67	0.04	0.14	1.64
HM15-3	0.23	0.62	13.63	70.65	0.20	4.54	8.30	0.05	0.13	1.62
HM15-4	0.24	0.66	13.80	70.29	0.19	4.54	8.53	0.05	0.14	1.63
HM15-5	0.27	0.62	13.83	70.02	0.24	4.49	8.70	0.05	0.14	1.64
LD7-1	0.51	0.88	13.37	69.87	0.35	3.71	10.00	0.05	0.12	1.14
LD7-2	0.49	0.84	13.14	70.19	0.35	3.80	9.90	0.05	0.11	1.14
LD7-3	0.45	0.80	13.29	70.02	0.34	3.76	10.02	0.05	0.11	1.16
LD7-4	0.46	0.82	13.37	69.83	0.33	3.77	10.10	0.05	0.11	1.17
LD7-5	0.45	0.81	13.28	69.95	0.35	3.80	10.04	0.05	0.11	1.17

Table 5: Huzhou original celadon enamel main chemical composition (100μm)

Sample	Na_2O	MgO	AL_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
Y1-1	0.66	1.35	18.43	72.12	0.50	2.90	1.36	0.52	0.07	2.10
Y1-2	0.47	1.20	16.64	68.36	0.78	3.13	0.85	0.18	0.06	8.33
Y1-3	0.42	1.64	16.73	59.91	2.17	1.47	13.18	0.25	0.28	3.99
Y1-4	0.38	1.27	19.49	63.98	0.84	1.92	8.09	0.30	0.12	3.59
Y1-5	0.58	1.11	22.51	68.74	0.47	3.38	0.86	0.27	0.05	2.51
Y2-1	0.60	1.85	15.39	61.11	1.38	1.66	13.99	0.37	0.28	3.40
Y2-2	0.59	1.46	18.86	64.28	0.69	2.83	4.46	0.47	0.13	6.23
Y2-3	0.52	1.51	16.51	73.67	0.40	2.71	2.53	0.46	0.05	1.56
Y2-4	0.55	1.69	14.12	53.82	1.76	1.34	23.81	0.34	0.12	2.48
Y2-5	0.46	1.36	17.19	67.90	0.56	3.35	3.57	0.55	0.06	4.90

5. Discussion of experimental results

5.1 Analysis of homogeneity of three kinds of celadon samples

Through the comparative analysis of Tables 2, 3, 4 and Table 5, especially the comparative analysis of the differences between Table 2 and Table 5, it can be seen that there is a significant change in the main chemical composition of different types of celadon under the beam diameter of 2 mm and 100 μm respectively, which is the primary chemical composition of the three types of celadon sample enamel under two conditions. Five different sites are tested under the same conditions for each sample and the data shows that the results of each measurement point in the same sample are similar with the beam spot diameter of 2 mm and that the results are significantly different with the beam spot diameter of 100 μm.

The standard deviation (SD) in statistics is a standard to measure the dispersion degree of data distribution, which can be used to measure the degree to which the data value deviates from the arithmetic mean. The smaller the standard deviation, the less the value deviating from the average value, and vice versa. The size of the standard deviation can be measured by the ratio of the standard deviation to the average value, which is the relative standard deviation (RSD). This value is usually used to indicate the precision of the analytical test results and the precision reflects the reproducibility of the measurement results. Table 6 shows the comparison of the relative standard deviation of the enamel element content of in the 10 celadon samples under the two beam spot conditions. It can be seen intuitively seen from this Table that the standard deviation at the spot diameter of 100 μm is several times or even ten times larger than that at the spot diameter of 2 mm. It is deduced that the spot diameter of 100 μm belongs to the micro area analysis. The tiny flaws in the sample enamel, including glaze impurities, bubbles, pores, and shrinkage spots that are difficult to see with the naked eye may lead to a significant change in the data. Therefore, the measured results cannot represent the overall elemental content of the enamel and sometimes even result in misunderstandings. In addition, this kind of relationship between the standard deviation of the sodium and magnesium elements in the individual sample in Table 6 is slightly less noticeable, which is related to the limitation of the EDXRF measurement method, the low content of the two elements and their low sensitivity.

Table 6: Comparison of relative standard deviations of element contents under different beam spot conditions

Sample	Na_2O	MgO	AL_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
Y1-1	17.76	11.08	5.87	0.89	12.56	3.43	18.54	1.36	16.67	14.59
Y2-1	3.37	1.96	5.41	4.88	29.49	16.37	55.08	4.40	8.67	9.33
P24-1	6.25	1.66	0.52	0.82	1.94	3.36	3.28	2.56	17.14	22.90
H1-1	1.92	3.35	1.91	8.54	2.10	4.17	7.04	3.52	32.09	8.5
JS3-1	4.13	3.36	0.88	0.94	2.56	3.42	8.69	1.85	8.90	9.19
YC6-1	4.73	0.41	1.05	0.84	6.74	2.97	4.41	3.36	3.57	4.69
YD6-1	4.35	5.50	1.51	0.87	5.76	3.58	4.75	5.38	4.34	0.71
HM15-1	7.66	5.80	1.31	6.37	26.83	0.98	4.75	10.65	2.82	2.43
LD7-1	3.20	4.18	1.25	1.84	9.77	2.08	37.49	0.00	5.51	2.37
ST15-1	7.10	7.01	1.55	2.76	25.13	0.93	5.33	12.54	0.00	2.56
ST17-1	5.34	9.98	1.04	0.60	11.45	1.27	14.70	11.91	4.03	0.51
SW15-1	9.36	3.81	0.71	1.51	15.66	0.98	5.28	0.00	3.99	1.31

It can be seen from the comparison of the above table that Huzhou original celadon, Yueyao Kiln and Longquan Kiln are distributed in three different regions and even the same celadon is also different due to different location of the kiln. The 5 data points in the same sample form a cluster, in which the STT15 and STT17 data points basically coincide with each other. It can be seen that under the conditions of the beam spot diameter of 2mm, the measurement results are stable and have good reproducibility. The data is credible and reflects the element content of the entire enamel, which will not cause interference and deviation for analysis and judgment. However, in the case of the beam spot diameter of 100 μm, although the three types of celadon are located in different sites, the boundary between them is not very obvious. Some sporadic data points will cross over to other areas, which may easily cause misjudgments. Especially, the sample data of the same type of sample in different kiln sites or in different years are mixed and disorganized, so it will be impossible to distinguish them, making it difficult to further analyze and determine the kiln sites, ages and minor technological differences of celadon.

6. Detection conditions and method selection

It can be seen from the above analysis that even though there are advanced instruments and equipment, if the detection conditions and detection methods are unreasonable, the results may be far from the authentic value, leading to wrong conclusions. Therefore, it is particularly important to scientifically select reasonable detection conditions and properly use appropriate detection methods. For the testing of enamel with mature technology like Longquan celadon under the condition of the beam spot diameter of 2mm, the impact of uniformity of the sample on the measurement result is not significant. The measurement result of various points are similar and the boundary of the three types of celadon enamel are obvious. If adopting the multi-point measurement method to obtain the average value, the result will be more reliable. Under the condition of the beam spot diameter of 100 μm, the multi-point measurement method must be used. Moreover, it cannot simply obtain the average of the multi-point measurement results, but to remover the abnormal data point and then to obtain the average value as the detection result. Otherwise, the data points are chaotic, which makes it impossible to distinguish different kiln and may even cause the misjudgment of the type of porcelain.

7. Conclusion

Through the analysis and discussion of the test results, the following conclusions can be drawn:
Under the condition of the beam spot diameter of 2mm, the results of the same sample at each measurement point are relatively similar. The factor load map shows that Huzhou original celadon, Yueyao celadon, and Longquan celadon are distributed in three different regions and there is even difference in the same celadon because of the difference of the kiln site. Under the conditions of the beam spot diameter of 100μm, the data of the five measurement points of the same sample are significantly different, which affects the correct judgment of the porcelain age, origin, and authenticity.
For the measurement of the original enamel, regardless of the size of beam spots, the measurer needs to carefully select each measurement point under the CCD magnified view and the measurement can only start when there is no shrinkage, cracking or spalling in the measurement point. Abnormal data points need to be removed from the measurement results then to obtain the average value.
When EDXRF is used to measure and analyze samples, firstly, it is necessary to select flat samples to reduce the error in the measurement result caused by the curved surface and to improve the accuracy of the data. Secondly, it is necessary to select the section on the sample surface with no corrosion and attachments for the measurement to reduce or even avoid the interference of the main component.

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