Analysis of chemical composition of ancient glass products based on grey correlation method

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Abstract. The Silk Road was the channel of cultural exchange between China and the West in ancient times, and the glass is the precious material evidence of early trade. Early glass was often made into bead-shaped ornaments and introduced into our country in West Asia and Egypt. After absorbing the technology, the ancient glass in our country was made locally. Although the appearance of the glass products was similar to the foreign ones, the chemical composition was different. Therefore, the analysis and identification of chemical composition is an important aspect to identify and study ancient glass products. In view of the different contents of weathering or non-weathering chemical components of different types of glass relics, this paper considers the types, patterns, colors, chemical components and other factors, and ignores environment-related factors, such as atmospheric environment, pH value, burial time, depth and other factors. Based on the existing data and relevant research results of domestic and foreign scholars, the classification rules of chemical components of high-potassium glass and lead-barium glass were obtained by using grey correlation analysis model, Chi-square test and improved weighted average algorithm. It is pointed out that the contents of SiO_2, K_2O, PbO and BaO should be observed in order to analyze and identify ancient glass products.

Keywords: Ancient glass, Chemical composition content, Grey correlation analysis, Correlation coefficient.

1. Introduction

The main raw material of glass is quartz sand, the main chemical composition is SiO_2. Due to the high melting point of pure quartz sand, in order to reduce the melting temperature, it is necessary to add flux during refining. Ancient commonly used fluxes are grass and wood ash, natural natron, saltpeter and lead ore, and add limestone as a stabilizer, limestone after calcination into CaO. The main chemical composition of the added flux is different. For half a century, ancient glass objects have been found in the excavations of ancient tombs in China, from the Western Zhou Dynasty, the Spring and Autumn Period, the Warring States period to the Tang, Song, Yuan, Ming and Qing Dynasties, providing important examples and materials for us to further study ancient Chinese glass [1].

Ancient glass is susceptible to weathering by burial conditions. During weathering, internal elements exchange a lot with environmental elements, resulting in changes in their composition proportions. Among them, lead-barium glass is easily weathered under the influence of burial environment, during which a large number of elements inside and in the environment are exchanged [2]. Gan Fuxi et al. concluded, through the experimental analysis of a large number of lead-barium glass unearthed in various places, that the development of ancient Chinese glass technology has its distinctive characteristics, among which lead-barium glass is a typical representative. It is believed that the origin of lead-barium glass manufacturing is related to the primitive porcelain and bronze smelting technology in ancient China [3, 4].

According to the research [5], it is found that at that time, the proportion of glass SiO_2, K_2O, Al_2O_3 is larger, because of the flux and production methods are different from those in the west. Therefore, for the high-potassium glass, relevant studies [6] show that most of the high-potassium glass unearthed in our country is most likely made with saltpeter as a fluxing agent or by using grass and wood ash by recrystallization and purification to remove the impurities such asMgO, CaO, etc., which results in the difference between some chemical compositions and early western glass.

The main research object of this paper is ancient glass relics. After hundreds of thousands of years, most of them buried underground will be damaged by chemical substances. Glass can be well preserved for several centuries in an environment without water, but there is a lot of water in the soil, and the reaction between glass and water will cause chemical changes on the surface of the glass and extend inward [7]. At the same time, on the basis of dividing glass relics into high-potassium glass relics and lead-barium glass relics by archeologists, the chemical composition and distribution of ancient glass products will be studied and discussed, ignoring the influence of environmental factors such as moisture and pH value after the excavation of these relics.

2. Materials and methods

2.1. Materials

2.1.1 Grey correlation analysis

Grey relation refers to the uncertain relation between things, or the uncertain relation between system factors and factors to the main behavior [8]. Grey correlation analysis is a method to describe the strength, magnitude and order of relations among factors by using grey correlation order [9] (grey correlation order for short). It is a method to analyze and determine the degree of influence among system factors or the measure of contribution of factors to the main behavior of the system through grey correlation degree. Its basic idea is: based on the data sequence of the factors, using mathematical methods to study the geometric correspondence between the factors, that is, the closer the geometric shape of the sequence curves, the greater the degree of grey correlation between them, and vice versa.

2.1.2 Chi-square test

The Chi-square test is a significance test that compares the difference between two or more sample rates (or ratios). When the difference between the compared samples is due to intrinsic factors rather than sampling error, the chi-square value is large, and the corresponding P-value reflecting the sample difference due to sampling error is less likely. Then the difference between the two samples is said to be "significant" or "highly significant". On the contrary, the smaller the chi-square value is, the larger the P-value is, which means that the difference between the two samples is "not significant" [10].

In essence, it is also the deviation degree between the actual observed value and the theoretical inferred value of statistical data, which is generally used to detect the difference between data.

2.1.3 Improved weighted average algorithm

Based on the weighted average algorithm, the standard normal distribution function is used in the weight algorithm:

$$f(x) = \frac{1}{\sqrt{2\pi}} e^{-\frac{x^2}{2}} \tag{1}$$

2.1.4 Correlation coefficient formula

$$roh = corr(date) \tag{2}$$

3. Process analysis, model building and solution

3.1. Grey correlation analysis, Chi-square test data processing and process analysis

According to the data given by the title, we know that different glass types, patterns, colors and surface differentiation have a certain relationship, and different weathering parts produce different chemical composition content. In this paper, the data are integrated, grey correlation analysis and Chi-square test are used to find the correlation and difference between surface differentiation and the other three factors. Since the data is more effective and accurate when the proportion of chemical components is accumulated and the balance is between 85% and 105%, the two data that the sum of chemical components is not between 85% and 105% are excluded. The data were screened and classified into four categories: high potassium weathering, high potassium weathering, lead barium weathering and lead barium weathering. Secondly, the weathering point detection data was also screened into four categories: high potassium weathering, high potassium weathering, lead barium undifferentiated, and lead barium differentiation. The weighted average algorithm was used to predict the chemical composition contents before weathering. There were 14 kinds of chemical composition contents, which were: $SiO_2, Na_2O, K_2O, CaO, MgO, Al_2O_3, Fe_2O_3, CuO, PbO, BaO, P_2O_5, SrO, SnO_2, SO_2$. τ_i(Predicted pre-weathering ratio of chemical composition at a weathering point) = $\varphi_i$weighted average of unweathering chemical composition (i=1,2...... 14).

Based on the given data, a grey relational analysis model is established to solve the correlation. With surface weathering as the parent sequence variable, type, pattern, color as the characteristic sequence variable, dimensionless processing was carried out for the data, resolution coefficient ρ=0.5. To solve the grey correlation value between the parent sequence and the feature sequence, the correlation coefficient is shown in Figure 1 below:

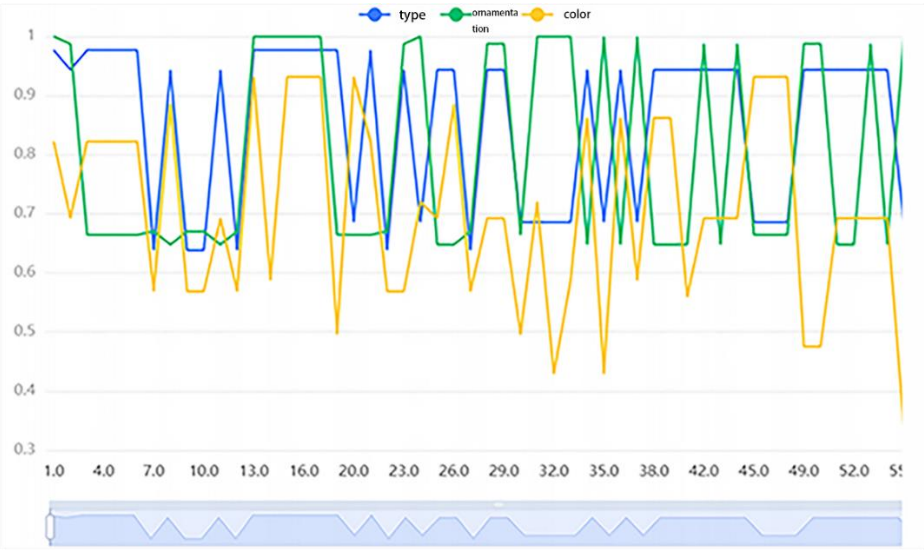

Figure 1. Grey correlation coefficient graph

Then the grey relational degree value is solved and the grey relational degree value is sorted. The correlation degree between type and surface weathering α=0.86, pattern and surface weathering β=0.795, color and surface weathering γ=0.702. It can be seen that type is the most correlated degree with surface differentiation, followed by pattern, and color is the least.

Secondly, Chi-square test is used to solve the difference (significance). The output Chi-square test analysis results are shown in Table 1 below:

Table 1. Chi-square test diagram

title	name	Surface weathering		total	X^2	correction X^2	P
		Weathering free	weathering				
ornamentation	A	11	11	22	4.957	4.957	0.084*
	B	0	6	6			
	C	13	17	30			
type	Lead barium	12	28	40	6.880	5.452	0.009***
	High potassium	12	6	18			

color	Nan	4	0	4	9.432	9.432	0.307
	Light green	1	2	3			
	Light blue	12	8	20			
	Dark green	4	3	7			
	Dark blue	0	2	2			
	purple	2	2	4			
	green	0	1	1			
	blue-green	9	6	15			
	black	2	0	2			

As can be seen from the figure, for surface weathering, the significance P value is 0.084*, which does not show significance at the level, and the original hypothesis is accepted. Therefore, there is no significant difference for surface weathering and decorative data.

For surface weathering, the significance P value is 0.009***, showing significance at the horizontal level, rejecting the null hypothesis, so there are significant differences for surface weathering and type data.

For surface weathering, the significance P value is 0.307*, which shows no significance at the level. The original hypothesis is accepted, so there is no significant difference for surface weathering and color data.

As for the statistics on the content of weathering chemical components on the surface of cultural relics samples, the average value of each chemical component in each category was taken and pie charts were drawn and summarized as Table 2,3:

Table 2. Four types of chemical composition content table

Types and types of glass Differentiation or not (percentage)	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3	CuO
High potassium differentiation	93.96	0	0.82	0.87	0.59	1.93	0.27	1.56
High potassium unweathered	67.03	2.73	9.62	6.4	1.24	6.35	2.11	2.45
Lead barium weathering	33.61	3.12	0.32	2.48	1.1	3.84	0.95	2.11
Lead barium is not weathered	53.44	3.34	0.42	1.46	0.91	3.19	2.02	1.84

Table 3. Four kinds of chemical composition content table followed by table

Types and types of glass Differentiation or not (percentage)	PbO	BaO	P_2O_5	SrO	SnO	SO_2	summation
High potassium differentiation	0	0	0.34	0	0	0	100.34
High potassium unweathered	0.59	1.03	1.33	0.08	1.18	0.41	102.55
Lead barium weathering	36.87	11.44	4.99	0.41	0.67	8.88	110.79
Lead barium is not weathered	23.59	10.5	1.07	0.48	0.42	3.66	106.34

To sum up, the statistical rule can be summarized as follows: In high potassium, the proportion of weathered SiO_2 is the largest, reaching 93.96%, and the rest of the components are generally less, among which the Al_2O_3 is 1.93%, and the proportion of Na_2O, SrO, SnO is 0.

In the high potassium content, non-weathered SO_2 accounts for 67.03%, followed by K_2O, CaO and Al_2O_3, accounting for 9.62%, 6.40% and 6.35%, respectively. Na_2O, Fe_2O_3 and P_2O_5 account for less, accounting for 2.73%, 2.11% and 1.33%, respectively. Other elements account for a small proportion.

In lead barium, the proportion of weathered PbO is 36.87%, followed by SiO_2 is 33.61%, BaO and SO_2 are 11.44% and 8.88% respectively, and other components account for a small proportion.

In lead barium, the proportion of non-weathered $SiO_2$is 53.44%, followed by PbO is 23.59%, $BaO$and $SO_2$are relatively small, 10.50% and 3.66%, respectively, and other components account for a small proportion.

Since the chemical composition content of different types of glass (high potassium glass and lead barium glass) and the sample detection points are different, there is a certain possibility that some chemical components are not detected, so there are many null values in the data (is 0.00).

Therefore, in order to predict the chemical content before weathering, we divided the data into four categories: high potassium weathering, high potassium weathering, lead barium undifferentiated, and lead barium differentiation. We assumed that the 14 chemical components in these four categories were x_j (j=1,2,......14), using MATLAB to implement weighted average algorithm, using standard normal distribution function $f(x)=\frac{1}{\sqrt{2\pi}}e^{-\frac{x^2}{2}}$ to carry out weight distribution in the weight algorithm, respectively to obtain the weighted average of the above four categories, and obtain the predicted values of different types of glass before weathering at different sampling points, as shown in Table 4 below:

Table 4. Some predicted pre-weathering data

type	number	Sampling point	$x_1 \dots$	x_9		$x_{10} \dots$	x_{14}
Lead barium	54	Severe weathering point	49.30	37.44		0.00	0.00
Lead barium	43	Site 2	55.76	25.56		2.99	0.00
Lead barium	51	Site 2	57.46	30.71		0.00	0.00
Lead barium	51	Site 1	56.75 …	20.62		7.36	0.00
Lead barium	8	Severe weathering point	17.52	27.41		41.54	2.63
Lead barium	26	Severe weathering point	13.76	24.59		46.80	2.71
Lead barium	43	Site 1	37.24	39.92		7.81	0.00
		……					
High potassium	7	Surface sampling	75.58805	0	0		0
High potassium	27	Surface sampling	73.81449	0	0		0
High potassium	9	Surface sampling	73.34773	0	0		0
High potassium	22	Surface sampling	59.92126	0	0		0
High potassium	12	Surface sampling	67.4564	0	0	……	0
High potassium	10	Surface sampling	74.47608	0	0		0

3.2. Classification law of high potassium glass and lead barium glass

The chemical content of the glass relics is the main basis, and the color, surface weathering and decoration of the relics are the auxiliary basis. According to the data, the maximum value of each chemical component of high potassium weathering, high potassium non-weathering, lead barium weathering and lead barium non-weathering was taken respectively, and the formation range was shown in Tables 5 and 6 below.

Table 5. High potassium glasspartial chemical composition content range

Chemical composition range of high potassium glass (unit: %)	SO_2	SnO_2	SrO	P_2O_5	BaO	PbO	CuO
Minimum and maximum values	0 0.47	0 2.36	0 0.12	0 4.5	0 2.86	0 1.62	0 5.09

Table 6. lead barium glass partial chemical composition content range

Content range of some chemical components of lead barium glass (unit: %)	SO_2	SnO_2	SrO	P_2O_5	BaO	PbO	CuO
Minimum and maximum values	0 15.59	0 1.31	0 1.12	0 14.13	0 35.45	9.3 70.21	0 10.57

In order to make the result more complete, the mean value, median value, variance and standard deviation of four kinds of chemical components were calculated as auxiliary data to summarize the rule.

Based on relevant data, the classification rules of high-potassium glass and lead-barium glass are as follows:

High potassium glass: whether weathered or unweathered, the proportion of potassium oxide is relatively high, the significant difference is large.

Lead barium glass: whether weathered or unweathered, lead oxide and barium oxide account for a relatively high proportion of significant difference.

4. Conclusion

To sum up, the main work of this paper is to analyze part of the chemical components of ancient glass unearthed relics according to part of their data, and summarize the rules and correlation. After contacting relevant information, we know that after glass was introduced into our country, our country uses its technology and local materials, adding different fluxes, and the main type of glass produced is high potassium glass and barium lead glass. The raw material for the production of these two kinds of glass is quartz sand, so both lead barium glass and high potassium glass silica components account for a large proportion. For high potassium glass, whether unweathered or weathered, the proportion of potassium oxide is relatively high because of the flux, grass and wood ash, etc. For lead-barium glass, the proportion of lead oxide and barium oxide is relatively high, whether weathered or unweathered, due to flux lead ore and other reasons. Based on the existing data, this paper mainly studies fourteen chemical compositions of ancient glass products, but the study of chemical compositions of ancient glass is a very complex and systematic work, which needs further study. Therefore, the remaining chemical composition of these two types of glass and the identification of the types of ancient glass products are also worthy of further exploration and study with the innovative idea of mathematical modeling.

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