Composition Analysis and Identification of Ancient Glass Products

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Abstract. Glass products are an important material evidence of the early trade exchanges between China and the West. Under the influence of buried environment, the weathering of glass leads to the change of its chemical composition proportion, which then affects the judgment of cultural relic category. This paper analyzes and identifies the components of ancient glass products by combining sample data. In order to analyze the influencing factors of weathering of cultural relics samples, the paper analyzes the high potassium and lead barium glass types and observes the relationship between the pattern and color of the sample, and the whole chi square independence test is used to obtain the difference rules of glass category, decoration and color classification. For the chemical composition content prediction, the prediction model was built and predicted by the sample mean difference. In this paper, the chemical composition of the unknown category of glass relics was analyzed and identified by training on the valid data in Form 2. For the sensitivity of the classification results, the sensitivity formula was applied to calculate a sensitivity of 0.125.

Keywords: Factor analysis method, K-means cluster, Fisher discrimination method, Gray association analysis.

1. Restatement of the problem

As a powerful material evidence of the trade along the early Silk Road in ancient China, the glass cultural relics have always been widely concerned by the archaeology circle. The internal chemical composition of the glass products is very different from the foreign products after the localization production [1-3]. The main component of glass products is silica (SiO_2), in the process of refining need to add flux and stabilizer such as plant ash and limestone, according to the main chemical composition of glass products is divided into lead barium glass and high potassium glass, the lead oxide (PbO), barium oxide (BaO) content is higher, potassium content in potassium glass is higher. In the process of burial, glass relics are susceptible to the influence of their local environment, which leads to different degrees of weathering [4-6]. In the process of weathering, the proportion of their internal components will change slightly, which will affect the archaeologists' judgment of the category of glass relics.

Analyze the relationship between glass type, decoration and color, combined with the type of glass relics, analyze the statistical law of weathered and weathered chemical content, and predict the chemical content before weathering according to the detection data of weathering [7]. According to the data of glass relics, analyze the classification rules of lead-barium glass and high potassium glass; select the appropriate chemical composition of the two categories, give the division method and results, and analyze the rationality and sensitivity of the results [8].

2. Problem analysis

Problem 1 To analyze the influencing factors of the surface weathering of glass relics, in this paper, the data in the attachment are quantified, and according to the type of high potassium and lead-barium glass classification analysis, respectively, the relationship between the surface weathering of glass relics and glass decoration and color and observation rules. Secondly, this paper also uses the chi-

square independence test from the overall data to conduct the factor analysis of surface weathering, and obtains the difference law of glass category, ornamentation and color classification.

Problem 2 based on the high potassium glass, lead barium glass classification data, this paper using factor analysis model of all kinds of chemical composition dimension reduction classification, through SPSS software to cultural relics sample data solution, according to the cumulative contribution rate and gravel diagram to determine the number of factors, calculate the rotating load matrix to determine the factor analysis model, and classify the various kinds of glass according to the number of factors [9].

Problem 3 this paper uses Fisher, uses form 2 as the training data, analyzes the chemical composition of unknown glass relics in form 3, and obtains the category identification results. For the sensitivity of the classification results in question 3, the silica content was also changed in Form 2, and the discriminant model was used to get a different result from the original classification results, and the sensitivity was calculated.

Problem 4 this paper uses the gray association analysis method to select high potassium, potassium oxide (K_2O) and lead-barium, lead oxide (PbO) as the reference sequences, and the rest of the chemical components are the subsequences. In the control group, high potassium lead oxide (PbO) and lead-barium potassium oxide (K_2O) were selected as the reference sequence. According to the line chart analysis of correlation degree and correlation degree, the difference of chemical composition correlation relationship between different categories was finally obtained [10].

3. Model hypothesis

Suppose that the surface weathering degree of the glass relic sample is independent of the time;
Assume that the chemical composition of the sample has an influence;
Assume that the sample data is true and accurate, without error;
Assume that the initial color of the sample is the same;
Assume that the sampling point in the sample replaces the overall chemical composition content.

4. Model establishment and solution

First, the data preprocessing was conducted. In this paper, the data in form 1 was quantified, and the value of the glass relic surface weathering, glass type, decoration and color was quantified, and the missing value was assigned to 0.

Through the analysis of the two types of glass relics samples of glass relics, the influence of glass decoration and glass color on the weathering can not be directly seen. In order to study the relationship between the weathering phenomenon of glass relics and the glass type, decoration and color as a whole, the chi-square independence test method is used to analyze the relationship:

First of all, the relationship between the weathering phenomenon of glass relics and the glass type is assumed:

H0: the weathering phenomenon of glass relics is independent of the type of glass, that is, the type of glass has no significant difference in the weathering of glass relics.

The alternative hypothesis is as follows:

H1: the weathering phenomenon of glass relics is different from the type of glass, that is, the type of glass is significantly different from the weathering of glass relics.

Similarly, the relationship between the weathering phenomenon of glass cultural relics and the glass decoration and color is assumed.

When the degree of freedom is 1 and the critical value is 0.05 when the confidence interval is 3.841, which is less than the calculation result 5.4, so the null hypothesis that the type of glass will affect the weathering of glass relics should be rejected.

The results can show that the glass type of glass is significantly different in the weathering of glass relics, and that the glass color indicates that the weathering of glass relics.

According to the problem background, the accumulation of components and data between 85% and 105% are regarded as valid data. First, the data in the attached form 2 are pre-processed, and finally the sample data of glass relics with number 15 and 17 is eliminated.

According to the statistics of the effective data in the attached form 2, this batch of glass relics are divided into four groups of high potassium weathered glass group, high potassium unweathered glass group, lead and barium weathered glass group and lead and barium unweathered glass group according to the category and weathering status, and the chemical composition content of each group of glass relics is analyzed.

In the high potassium weathered glass, Al_2O_3 and CuO, Fe_2O_3 and P_2O_5 are less abundant, and MgO and Fe_2O_3 are relatively stable.

There are more chemical components K_2O and Al_2O_3, less PbO and SO_2, and more stable Na_2O and MgO.

The chemical contents of PbO and BaO, Na_2O and Fe_2O_3 are less abundant, and CaO and Al_2O_3 are relatively stable.

The chemical components of PbO and BaO, MgO and Fe_2O_3 are less abundant, and CaO and Fe_2O_3 are relatively stable.

In order to construct a reasonable prediction model, the prediction model is established based on the sample mean difference. Firstly, the average difference between the weathered and unweathered chemical components of high-potassium glass and lead-barium glass cultural relics is calculated as follows:

$$\Delta \bar{x}_i = \bar{a}_i - \bar{b}_i \tag{1}$$

After obtaining the average difference between the chemical composition content of high-potassium glass and lead-barium glass relics respectively, the chemical composition content of the weathering of glass relics is predicted, and the calculation formula is as follows:

$$e_i = \Delta \bar{x}_i + O_i \tag{2}$$

In order to analyze the classification rules of high-potassium glass and lead-barium glass, factor analysis was used to reduce the dimension of two types of effective data in annex form 2, and finally, four factors and their corresponding scores were selected.

The main characteristics of this glass type can be expressed by 14 chemical composition indicators, which are 14 chemical components in Annex Form 2. Establish a correlation matrix for these 14 indicators (see support materials for details of high potassium and lead barium):

The eigenvalue λ of the correlation matrix R is calculated and arranged in the order from large to small, and then the information contribution rate and the cumulative contribution rate of each principal component are calculated. The formula is:

$$c_j = \frac{\lambda_j}{\sum_{k=1}^{14} \lambda_k}, \ j = 1,2,...14 \tag{3}$$

In order to determine the number of main factors more reasonably, a gravel test was introduced on the basis of comparing the cumulative contribution rate. Through SPSS, the software generated a gravel map of 14 factors as shown in Figure 1:

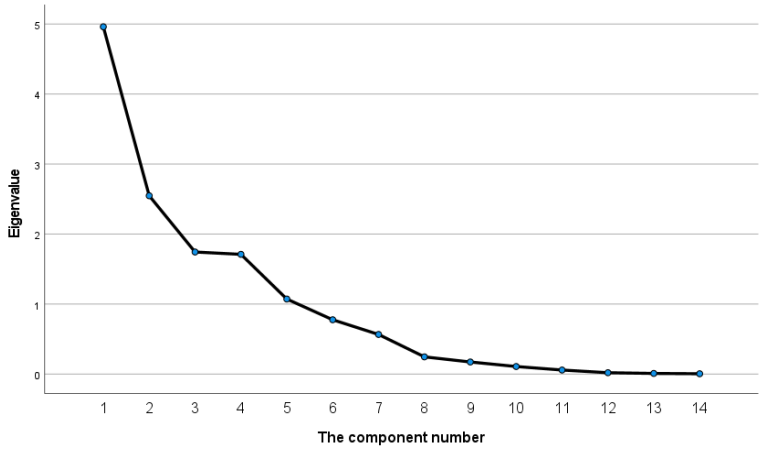


Figure 1. A rubble plot of the eigenvalues

Figure 1 shows that the change of eigenvalue corresponding to the first four factors is relatively steep. Starting from the fifth factor, the change of eigenvalue is relatively flat, and the cumulative contribution rate of the first four factors has reached 83.205%. Therefore, the four factors are selected in this paper.

The correlation matrix R of the lead-barium glass is calculated from the same method and steps, that is, the eigenvalue and the cumulative contribution rate of each principal component, and the factor load matrix A after rotation. The classification coefficient of each factor principal component can be obtained from the load matrix. It can be seen that lead oxide and barium oxide are in the same class, and silica and potassium elements are in the same class, showing the chemical composition classification law of high potassium glass. The classification of the chemical composition continues below.

Based on the results analysis, the significance was less than 0.01, indicating a correlation between the raw variables, and rejecting the null hypothesis at a 95% confidence level, meaning that the data were considered suitable for factor analysis.

Now the 14 sample points are clustered by K-means method. All sample points are clustered into 4 categories through the previous analysis and selection, and 4 cluster centers are initialized, and the distance between each sample point is calculated using the cluster center.

For the rationality analysis of the classification results, the factor analysis method finally determines the number of factors to ensure the robustness, objectivity and rationality of the clusters, and rotates the load matrix to ensure the universality and accuracy of the results.

To test the sensitivity of the cluster analysis results, this paper studied high potassium glass samples. Since silica is the main component of glass relics, three silica components were randomly selected to modify them, and we use factor analysis and cluster analysis again to obtain the modified cluster results as follows.

Category I is lead oxide (PbO), barium oxide (BaO); silica (SiO_2), magnesium oxide (MgO), alumina (Al_2O_3), iron oxide (Fe_2O_3), copper oxide (CuO), phosphorus pentoxide (P_2O_5), strontium oxide (SrO), sulfur dioxide (SO_2); sodium oxide (Na_2O), potassium oxide (K_2O), calcium oxide (CaO); and tin oxide (SnO_2).

The new clustering results compared the original cluster results, indicating the high sensitivity of high potassium glass classification results. Similarly, the lead-barium glass samples were studied, the three silica components were randomly selected and modified, and the factor analysis and cluster analysis were used again, and the modified cluster results were also compared with the original cluster results, indicating that the sensitivity of the high potassium glass classification results was high.

It was trained by the SPSS software using the data in the attached form 2 to Fisher identify the eight unknown samples in the form 3.

The value of 0 indicates the type of high potassium glass, and the value of 1 indicates the type of lead-barium glass. The chemical composition analysis of 8 unknown categories of glass relics are shown in Table 1:

Table 1. Identification results of glass relics of unknown categories

Sample number	A1	A2	A3	A4	A5	A6	A7	A8
Identify the value	0	1	1	1	1	0	0	1
Type	High potassium	Lead barium	Lead barium	Lead barium	Lead barium	High potassium	High potassium	Lead barium

After increasing the proportion of the silica content of the trained data in the Fisher discrimination model by 10, the discrimination calculation is calculated again. The sensitivity formula is used to calculate the ratio of the discrimination result and the original result. The formula is:

$$\sigma = \frac{m}{M} \tag{4}$$

Where, σ is the sensitivity, m is the number of changes in the judgment results, M is the number of original discrimination results.

Grey association analysis is used to analyze different types of glass samples. It can be seen from the material that the content of potassium in high-potassium glass relics is high, and lead oxide (PbO) and barium oxide (BaO) in lead and barium glass relics. Therefore, chemical potassium oxide (K_2O) is selected as the reference sequence, and chemical lead oxide in lead and barium glass samples (PbO) is selected as the reference sequence. Since the main component of glass relics is silica (SiO_2), the analysis of its association with other chemical components is no longer considered.

The analysis sequence consists of the reference sequence and the comparison sequence, where the reference sequence is the data sequence reflecting the system behavior characteristics, recorded as c_0; the comparison sequence consists of the factors affecting the system behavior, recorded as (c_1,c_2,...,c_m); the number of data items is recorded as n, Taking the high potassium glass cultural relic sample as an example, the chemical component potassium oxide (K_2O) was selected as the reference sequence, and after removing the main chemical component of silicon dioxide (SiO_2), the remaining 12 chemical components were used as the comparison sequence.

To narrow the metric range to simplify the computation, the data was first preprocessed. The mean of each index is calculated, and each element in the index is taken as the mean of the index separately.

Tin oxide (SnO_2), strontium oxide (SrO), iron oxide (Fe_2O_3) have the highest correlation with potassium oxide (K_2O), indicating that the content of these three chemical components has the greatest impact on the content of potassium oxide (K_2O).

Barium oxide (BaO), alumina (Al_2O_3), and phosphorus pentoxide (P_2O_5) have the highest correlation with lead oxide (PbO), indicating that the content of these three chemical components has the greatest influence on the content of lead oxide (PbO).

To compare the correlation between chemical components of different categories, calculate the correlation of gray correlation of other high potassium glass artifacts and potassium oxide (K_2O), other chemical components and lead oxide (PbO), the gray correlation of high potassium glass artifacts and lead oxide (PbO), and other chemical components and potassium oxide (K_2O) as a control group. As shown in Figure 2-4.

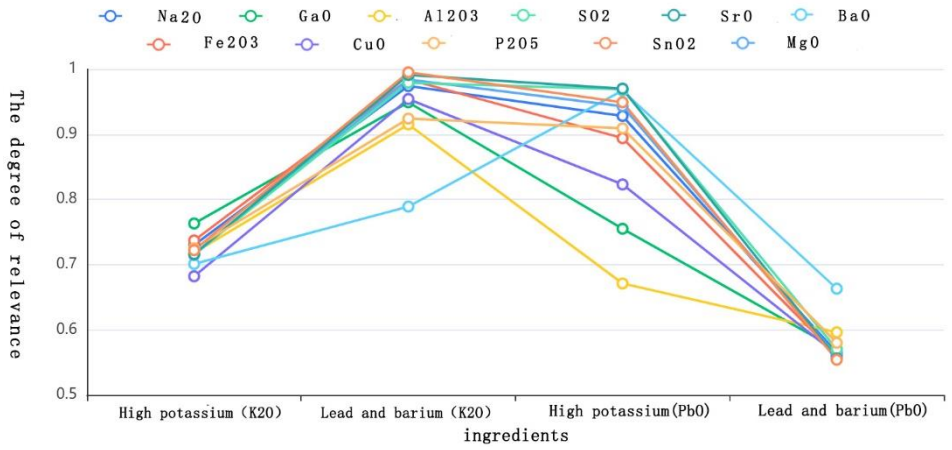


Figure 2. Line plot of the chemical composition correlation degree

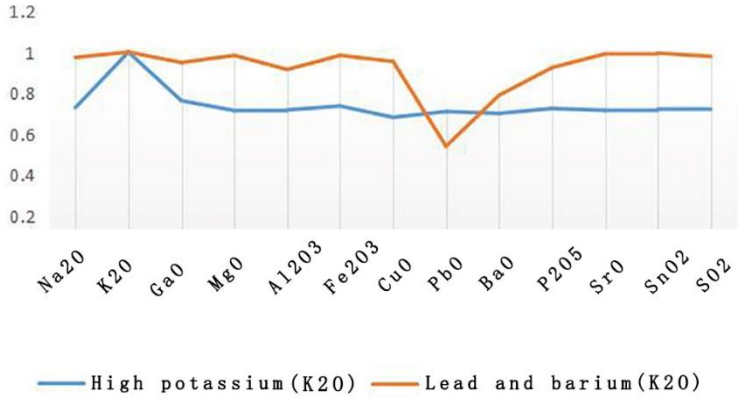


Figure 3. Line plot of the association degree of potassium oxide in high potassium and lead barium

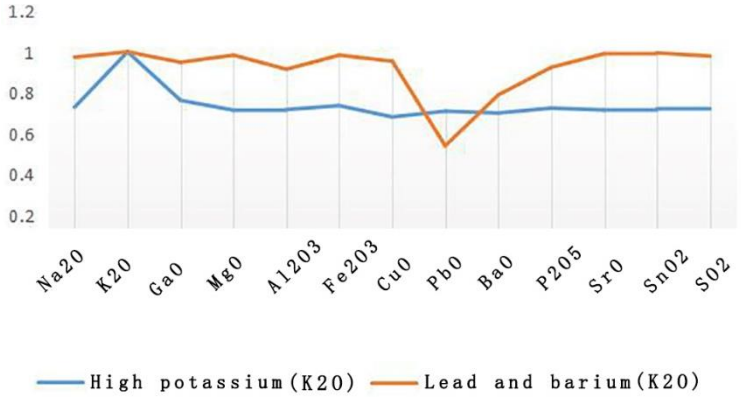


Figure 4. Line plot of the correlation degree of lead oxide in high potassium and lead barium

In the correlation analysis of lead oxide in high potassium and barium, alumina (Al_2O_3), lead oxide (PbO), lead oxide (PbO), is high correlation of tin oxide (SnO_2), high potassium glass relics, and lead oxide (PbO), and lead oxide (PbO) of lead-barium glass relics.

It can be seen from the correlation degree of potassium oxide (CaO) of potassium oxide (K_2O), and potassium oxide (K_2O) of copper oxide (CuO) and high potassium glass relics, potassium oxide (K_2O), and potassium oxide (K_2O) of lead-barium glass relics.

The above analysis showed significant differences in the chemical associations between high potassium and lead-barium glass categories.

5. Conclusion

Advantages of models: The mathematical models used in this paper are based on mature theories and have extremely high confidence. The model is closely related to the practical problems, and it

has a high practical value. As at problem 1, in order to analyze the relationship between the surface weathering of glass relics and its glass type, pattern and color, the method of chi-square independence test is adopted to make the analysis conclusion universal. To predict the chemical composition content of glass relics before weathering, the prediction model of preweathering chemical composition content is constructed according to the sample mean difference, and all the sample data are used to make the prediction results robust. For the problem 2, this paper adopts the factor analysis method to analyze the classification rules of the two types of glass, determines the final number of factors, and ensures the objectivity and rationality of the cluster number, and adopts the K-mean method for the subclass classification to make the results more universal. For problem 3, the Fisher identification method was selected for training and used to identify the types of unknown categories of glass relics. The identification results have high reliability.

The disadvantages of the model are due in the factor analysis of the chemical composition of different categories of glass relics samples, the selection of reference sequence is more subjective, which makes the objectivity of the analysis conclusion weak.

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Promotion of model: The Fisher discriminant model constructed in this paper to identify the types of unknown categories of glass relics has high practicability. By modifying the sample type and replacing the training data, it can be extended to food conformity inspection and material category identification.

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