

Research on Composition Analysis Identification and Protection of Ancient Glass Products based on FCM

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Abstract

After flowing into China along the Silk Road, glass has been circulating in the local territory for thousands of years. In the process of smelting, craftsmen of successive dynasties added different cosolvents, and the composition structure has its own characteristics. By studying the composition and material changes of ancient glass relics, it can provide theoretical support for archeologists to analyze the background of glass unearthed relics, which is of great research value. In this paper, the composition identification and analysis of ancient glass components were taken as the research objective, and different kinds of glass were divided according to different chemical compositions and organizational structures. Influencing factors and countermeasures of glass cultural relics weathering over the years; Further study on the protection of Chinese glass relics. Using correlation analysis, principal component analysis, FCM fuzzy clustering and other methods to analyze the above problems, and draw a conclusion. The innovation of this paper is to pretreat the ancient glass conditions and quantize the features to show the visual diagram; A variety of clustering models are established to ensure the accuracy of the conclusions. Considering the research problem in combination with the actual situation, the sub-classification situation has more practical reference value: both error analysis and sensitivity analysis are taken into account to ensure the reliability of the research.

Keywords

Ancient Glass; Component Analysis and Identification; Cluster Analysis; Preservation of Glass Artifacts.

1. Introduction

Modern glass can be seen everywhere in industrial buildings, art statues, photoelectric industry and other industries, but the development of Chinese traditional glass technology is very bumpy. Chinese traditional glass has been fully integrated with China and the West for thousands of years, showing various development trends and forming a huge glass system. To study the unearthed glass relics is helpful for archaeologists to fully investigate the aesthetic orientation and technological level of each dynasty. However, Chinese archaeologists still have some problems in the analysis of the composition of ancient glass products. The diversity of glass species and cultural fault lines have brought great challenges to archeologists.

Starting from the chemical composition of glass, this paper studies the chemical composition characteristics and classification basis of a batch of unearthed glass relics, and obtains the basis for the analysis and identification of ancient glass and the protection method of glass relics from the weathering of glass and the unearthed situation of cultural relics in various places, providing new ideas and theoretical support for the analysis and protection of Chinese glass in the archaeological circle.

By referring to the relevant research results of Chinese and foreign scholars, the author found that Guo Xiaoyan proved that Chinese traditional glass making process experienced local production and the introduction of foreign technology, forming a unique artistic process from three dimensions of time, region and cultural exchange [1]. Archaeologist An Jiayao concluded from the changes in the composition of glass beads that a relatively complete lead-barium glass industry had been established in China during the Warring States Period. In addition, glass utensils of different shapes in different dynasties also contain profound historical background [2]. Tong Zhifang et al. proved that the change of FeO content would affect the occurrence, distribution, migration behavior and chromium fixation effect of Cr in glass-ceramics, and expounded the influence of chemical composition change on glass from another perspective [3]. Wen Rui et al. used laser Raman and other methods to conduct spectral imaging of cultural relics in a site group in Xinjiang, and confirmed that these cultural relics unearthed in the late Warring States period were soda-calcium glass system [4].

From the research of foreign experts, it is concluded that the raw materials used for coloring glass are most likely from the residue of bronze smelting. Y.j. Masse et al. studied a batch of glass relics in the period of the new king of Egypt and found that the color of glass is proportional to the content of chemical composition, and some colorants are by-products produced by bronze smelting. The connection between glass making and bronze smelting has been confirmed.

2. Research Methods and Data

In the process of research, the whole involves three parts, which are chemical composition analysis of ancient glass relics, identification analysis of ancient glass types and excavation and protection of glass relics. This paper takes fuzzy clustering algorithm as the core to conduct in-depth analysis of chemical components. See Figure 1 for the research ideas and methods.

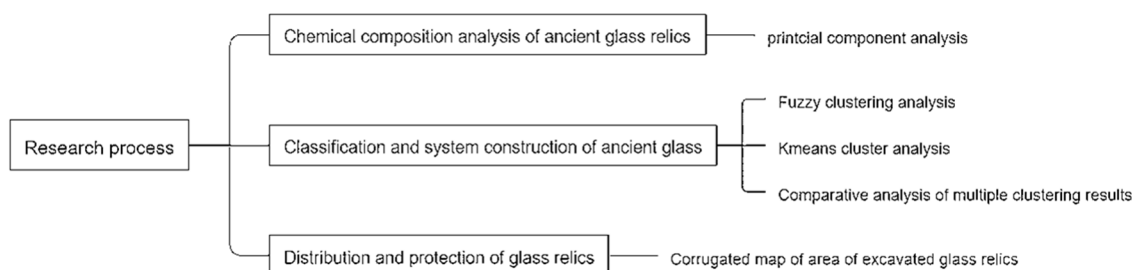


Figure 1. Conceptual framework

In this paper, when the ancient glass categories are studied, the chemical composition of the glass relics is analyzed first, the original data is pretreated, and the invalid data is cleaned. Secondly, different kinds of glass are classified according to the distribution characteristics of chemical composition. Collate the existing data and conduct cluster analysis. Then, the accuracy of subdivision of glass types is divided from macro and micro perspectives. At last, some suggestions on the protection of Chinese glass relics are put forward.

The data in this paper are from the attached data of Question C of the 2022 Mathematical Contest in Modeling for Chinese College Students.

3. Empirical Research

3.1. Chemical Composition Analysis of Ancient Glass Relics

In this paper, the chemical composition of this batch of glass relics will be analyzed, and the general distribution of different kinds of glass will be observed from the perspective of composition.

From the figure, we compare the general distribution of chemical components of high-potassium glass and lead-barium glass, and it can be found that except for SiO₂, the main components of glass, the contents of PbO, BaO, P₂O₅, Al₂O₃, CaO and K₂O are relatively large. The content of BaO and PbO is much higher than that of other chemical components. After careful comparison, it can be found that the K₂O of high potassium glass is more. In addition, lead barium glass also contains a large amount of BaO, PbO, and the content is far more than K₂O.

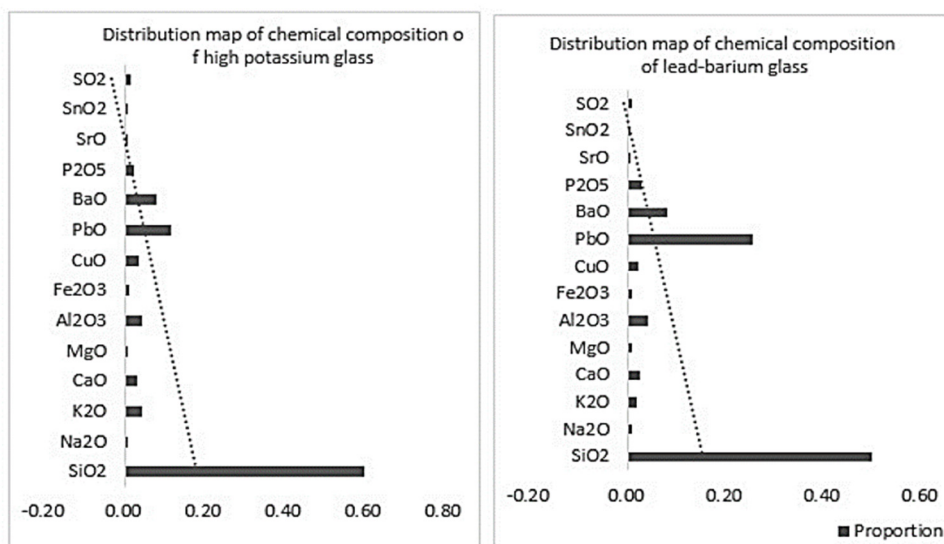


Figure 2. Distribution map of chemical composition of glass

3.2. Glass Classification and Classification System Construction

Table 1. Table of one-way analysis of variance

Server variable	Sample size	Average	Standard deviation	F	P
SiO ₂	67	49.022	24.316	60.284	0.000***
Na ₂ O	67	0.786	1.653	0.936	0.337
K ₂ O	67	1.847	3.879	68.781	0.000***
CaO	67	2.532	2.325	8.772	0.004***
MgO	67	0.683	0.65	0.602	0.441
Al ₂ O ₃	67	4.041	3.067	2.773	0.101
Fe ₂ O ₃	67	0.849	1.179	5.229	0.025**
CuO	67	1.954	2.242	0.197	0.659
PbO	67	24.463	19.513	87.247	0.000***
BaO	67	7.779	8.425	26.06	0.000***
P ₂ O ₅	67	2.684	3.544	5.762	0.019**
SnO ₂	67	0.078	0.337	0.612	0.437
SrO	67	0.262	0.267	26.064	0.000***
SO ₂	67	0.603	2.698	0.968	0.329

After exploring the classification basis of high-potassium glass and lead-barium glass, this paper improves the classification system on this basis, which will provide more detailed and specific classification and classification basis of glass varieties in cultural relics. We will establish a classification regression function to seek the main variables that affect the division of high potassium glass and lead barium glass by step recursion, and find the classification basis. In addition, in order to ensure the practical significance of the experimental study, the author will subdivide the two types of glass from macro and micro perspectives, use a variety of clustering methods to repeatedly classify the data to ensure the rationality of classification, adjust the sensitivity of parameter test, finally determine the number of classifications and improve the classification system of glass.

In this paper, the regression model is used to study the degree of influence of different chemical components on the classification of glass. The high-potassium glass is set as 1, and the lead-barium glass as 0 as the classification variables of order characteristics. By controlling the changes of various chemical components in the regression equation, the AIC value is observed and the optimal variable is retained.

Among the 14 groups of chemical components, some chemical components are irrelevant to the type of glass. In order to eliminate the influence of irrelevant variables on regression, variance analysis is used to carry out variable retention. Most of the variables had low correlation, so one-way analysis of variance was used.

As can be seen from the above table, SiO_2 , K_2O , CaO , Fe_2O_3 , PbO , BaO , P_2O_5 and SrO have significant differences in chemical compositions among different glass types because the p value is less than 0.05 in the single factor analysis, so the above variables are retained. It is speculated that the chemical composition of these variables will affect the classification of glass. SiO_2 , K_2O , CaO , Fe_2O_3 , PbO , BaO , P_2O_5 and SrO will be fitted with the type of glass.

In order to extract the main variables, this paper reduced the dimension of selected variables. The main purpose of variable dimension reduction is also to reduce the number of independent variables. Different from direct screening, variable dimension reduction through principal component analysis can not only simplify variables, but also not lose too much information. The principal component factor between eight variables should be extracted to represent all relevant variables when the two types of glass are divided into subclasses.

Table 2. KMO and Bartlett Test List

		High potassium	Lead-Barium
KMO-Sampling suitability quantity		0.843	0.712
	Approximate chi square	113.324	213.241
Bartlett Test List	Degree of Freedom	28	28
	Statistical significance	0	0

When the KMO sampling test value is close to 1, it indicates that the factor analysis effect is better; when the KMO value is less than 0.5, it is not suitable for factor analysis; When the principal component extraction results of the samples of known data belong to the type, the KMO value is greater than 0.7, and the factor analysis effect is better. Through the principal component method to extract the variance of each variable, this paper thinks that most of the extraction effect is very good.

The following table shows the extraction of principal component factors in high potassium glass. Two factors are extracted from eight chemical components of high potassium glass. These two factors explain 82.579% of the total variance of variables involved in dimension reduction,

indicating that these two principal components can represent the influence of the original eight indexes on glass classification.

Table 3. Total Variance Explanation Table (High potassium glass)

Element	Initial Eigenvalues			Extract the sum of loads squared		
	Aggregate	Percentage of variance	Accumulate	Aggregate	Percentage of variance	Accumulate
1	3.571	49.413	49.413	3.571	49.413	49.413
2	1.538	33.166	82.579	1.538	33.166	82.579
3	1.288	10.096	92.675			
4	1.038	4.975	97.650			
5	0.344	2.102	99.752			
6	0.208	0.074	99.826			
7	0.035	0.136	99.962			
8	0.013	0.038	100			

Two factors were extracted from eight chemical components of lead-barium glass. These two factors explain 83.850% of the total variance of variables involved in dimension reduction, indicating that these two principal components can represent the influence of the original eight indexes on glass classification.

Table 4. Total Variance Explanation Table (Lead barium glass)

Element	Initial Eigenvalues			Extract the sum of loads squared		
	Aggregate	Percentage of variance	Accumulate	Aggregate	Percentage of variance	Accumulate
1	3.281	63.332	63.332	3.281	63.332	63.332
2	1.641	20.518	83.850	1.641	20.518	83.850
3	1.169	10.621	94.471			
4	1.032	3.765	98.236			
5	0.771	1.381	99.617			
6	0.518	0.282	99.899			
7	0.338	0.053	99.952			
8	0.015	0.048	100			

Table 5. Principal component matrix

	High potassium glass		Lead barium glass	
	1	2	1	2
SiO ₂	0.972	0.066	0.912	0.314
K ₂ O	0.864	0.462	0.630	0.1112
CaO	0.812	-0.475	0.764	-0.168
Fe ₂ O ₃	0.789	-0.301	0.731	0.456
PbO	0.459	0.867	0.11	0.821
BaO	0.172	0.078	0.096	-0.697
P ₂ O ₅	0.51	0.211	0.046	0.356
SrO ₂	0.385	-0.546	-0.151	0.248

According to the total variance interpretation rate, we can find that the difference contribution rate of lead barium glass is relatively high, which can reach more than 83%. Next we will use the component matrix to find the main representative variables in the principal component.

According to the composition matrix, two principal components were extracted from high potassium glass. The first principal component factor mainly composed of SiO₂ and K₂O. The second principal component factor is P₂O₅ and SrO₂. According to the composition matrix, two principal components are extracted from lead-barium glass. The first principal component factor mainly consists of SiO₂ and K₂O. The second principal component factor mainly consists of PbO and BaO. This variable dimension reduction.

After that, we will use the newly generated principal component factors y1 and y2 for clustering. The basic formula of the model is as follows:

$$y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \beta_3x_3 + \dots + \beta_nx_n \tag{1}$$

In this model as the dependent variable y classification variables, namely β_0 as the constant, β x represents different composition proportion of chemical products, including greater influence to classification variables variables have certain effect. Through one-way analysis of variance, we can timely know the relationship between independent variables and dependent variables, so as to retain important correlation variables. Stop after model iteration step 7, at this time of the AIC = 6 to the minimum.

$$y = 154.8x_9 \pm 1083.2x_{13} - 1377.2 \tag{2}$$

Due to the given conditions and the actual situation, the variables retained during the four steps of iteration were taken as the directly related variables: the final retained variables K₂O, SrO, BaO and PbO. Therefore, the classification basis for distinguishing the two kinds of glass was the proportion of the above four chemical components. BaO and PbO were given priority, followed by K₂O.

$$y = -67.531x_3 + 3.686x_9 + 3.818x_{10} + 33.038x_{13} - 32.087 \tag{3}$$

In the test of fit degree, the coefficient of determination is an important standard for testing the fitting degree of sample regression line. Generally speaking, the closer the coefficient of determination is to 1, the better the fitting effect will be.

Table 6. Table of determinable coefficients

coefficient of determination	R2
Cox-Snell R2= 0.7018679	0.713

In general, the value of the pseudo-determination coefficient is smaller than the determination coefficient, Cox-Snell R2=0.713, which proves that the degree of fitting is good and the variable selection is correct. The content ratio of K₂O, SrO, BaO and PbO in glass is the main factor affecting the classification of glass.

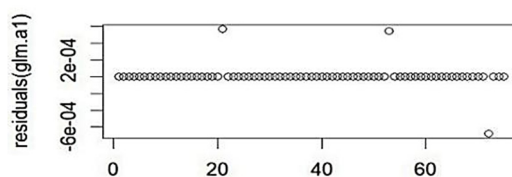


Figure 3. Regression residuals

In order to reflect the visually, we made a regression residual graph, from which we can see that the mean of residual error is 0, and the residuals are randomly and evenly distributed on

both sides of $n/1.414$. There is no excess information contained in the residual error, and the information is sufficiently extracted. The four variables we extracted can fully classify glass.

Fuzzy clustering (FCM) is a kind of clustering algorithm. The basic idea of fuzzy clustering is to ensure that the similarity between the same cluster is the highest, while the similarity between different clusters is the lowest. Fuzzy clustering belongs to soft clustering algorithm, which gives more weight to the object and more space for classification, and can make good classification errors. In order to ensure the objectivity and practicality of the classification results, fuzzy clustering was selected to establish the glass classification system during the preliminary construction of the classification system.

In this study, we will make sub-classification of high-potassium and lead-barium glass respectively. Due to the excessive design dimensions of variables, it is easy to generate noise in the process of exploration, which will interfere with the experimental results. Therefore, we propose to divide the perspective into macro level and micro level. The macro level is visible to the naked eye: color, texture, weathering or not. Microscopic level: chemical composition. When $K=2$ is obtained by contour coefficient, it is the most suitable. Therefore, each category is divided into two sub-categories.

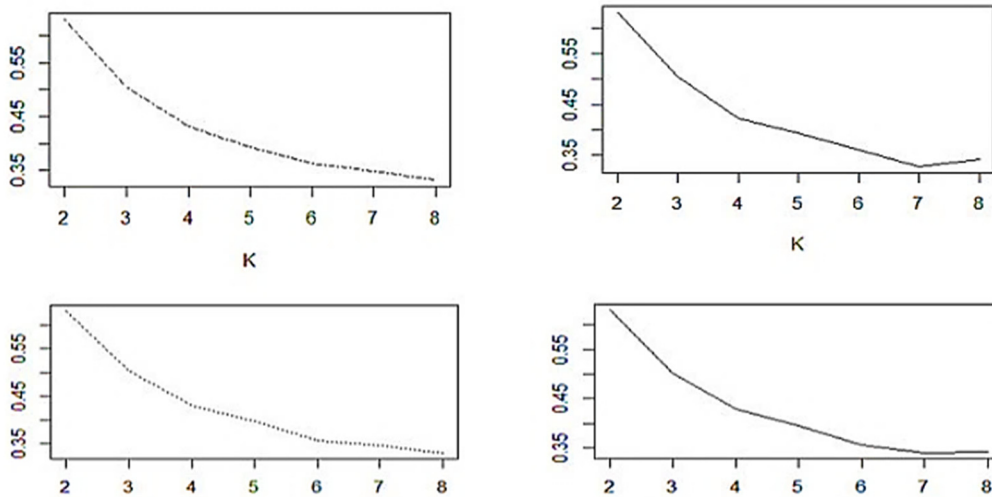


Figure 4. Contour coefficient diagram

The specific situation of clustering is as follows:

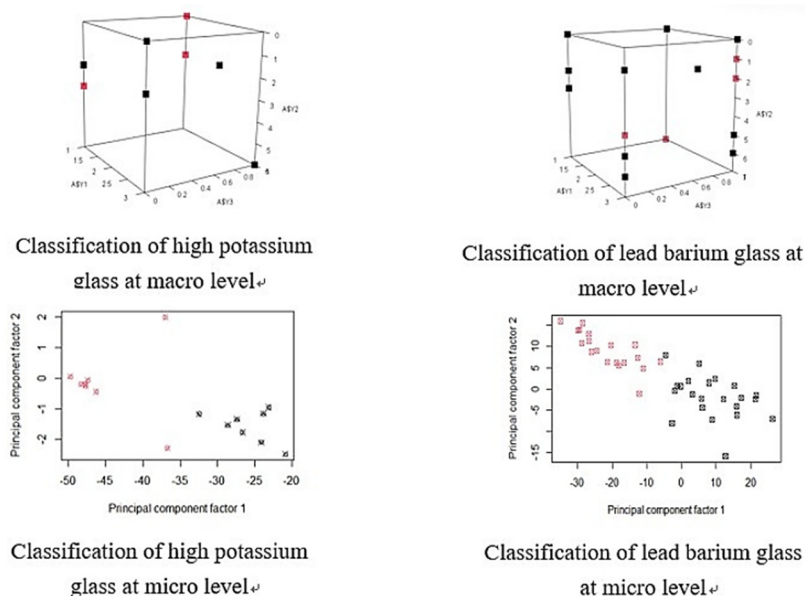


Figure 5. Cluster diagram of glass subclassification

Micro-high potassium glass: x_1 mainly contains SiO_2 , K_2O , x_2 mainly contains PbO ; Microscopic lead-barium glass: x_1 mainly contains SiO_2 , K_2O , x_2 mainly contains BaO ; Macro types of glass: x_1 for decoration, x_2 for color, x_3 for the degree of differentiation.

Classification basis: When classifying high-potassium glass at the microscopic level, it is divided according to the content of main components. The higher the internal potassium content, the closer it is to grade A, and the higher the internal barium content, the closer it is to grade B. At the microscopic level, lead barium glass is classified according to the content of main components. The higher the internal lead content, the closer it is to grade A, and the higher the internal potassium content, the closer it is to grade B. The classification of glass at the macro level is divided according to the degree of weathering and the depth of color. The more severe the degree of weathering, the darker the color, the closer to grade B, and vice versa.

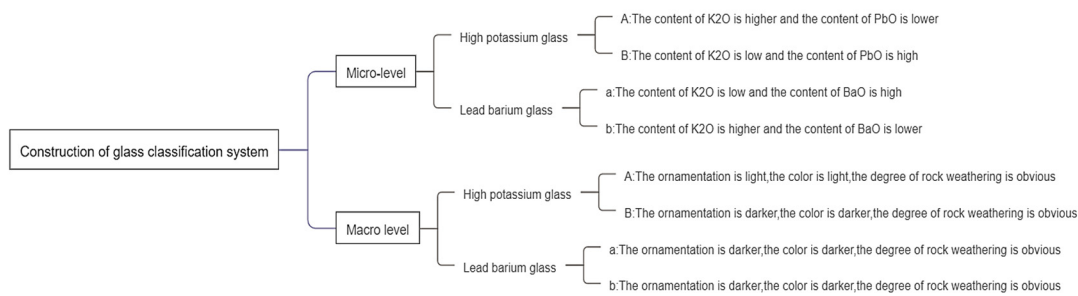


Figure 6. The result of glass classification

In order to ensure reasonable and accurate data clustering results, we simultaneously used Kmeans clustering and MINIBatchkmeans clustering to conduct secondary clustering analysis on the processed data, and compared it with the clustering graph obtained by fuzzy clustering to confirm the accuracy of the clustering results. In order to ensure the rationality of the verification, this paper adopts simple random sampling to select part of the data sets for comparison. The results are as follows (K=2) :

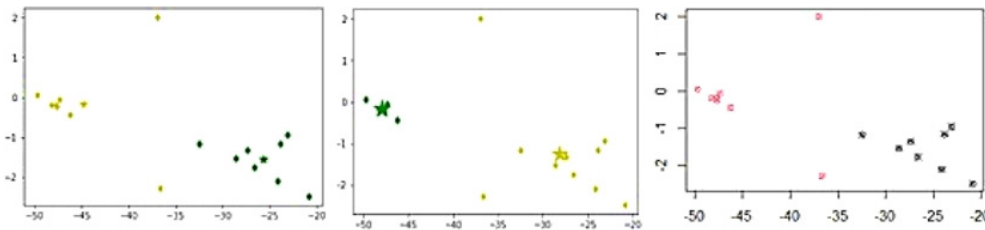


Figure 7. Macro high potassium data set

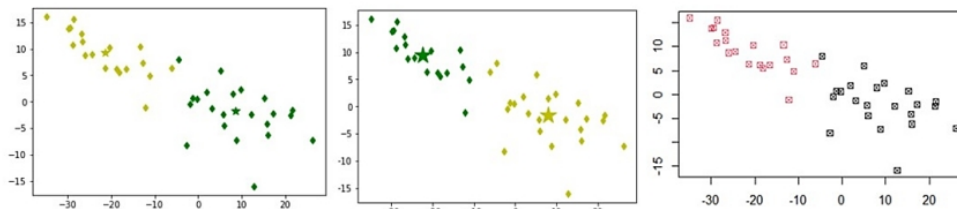


Figure 8. Macro lead barium data set

By comparison, K-means clustering, MiniBatchkmeans clustering and FCM fuzzy clustering have the same distribution for the same data clustering class graph. Therefore, the result of FCM fuzzy clustering is reasonable and reliable.

K=2 was determined by the contour coefficient, but the contour coefficient could not accurately reflect the optimal value of K, so several groups of data were randomly selected and the

clustering situation was observed by constantly changing the value of k value parameter. (From left to right, K=2,K=3, K=4)

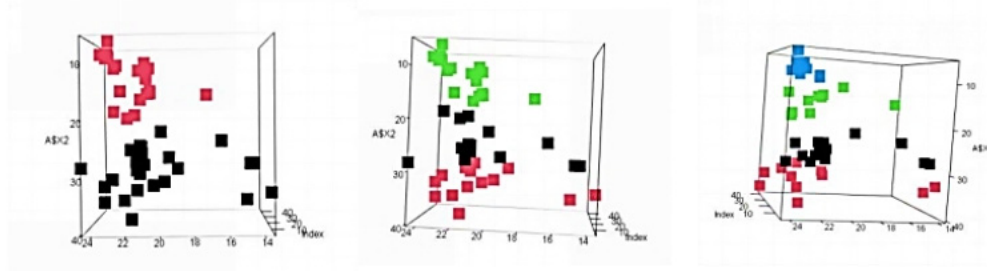


Figure 9. Cluster graph (K=n)

3.3. Identification Analysis of Ancient Glass Species

For the identification and analysis of ancient glass, the whole data set will be processed by cluster analysis, and the unknown data will be classified. In the process of clustering processing, the pre-processed data set is integrated with some unknown data to ensure the same classification basis.

The following is the clustering situation:

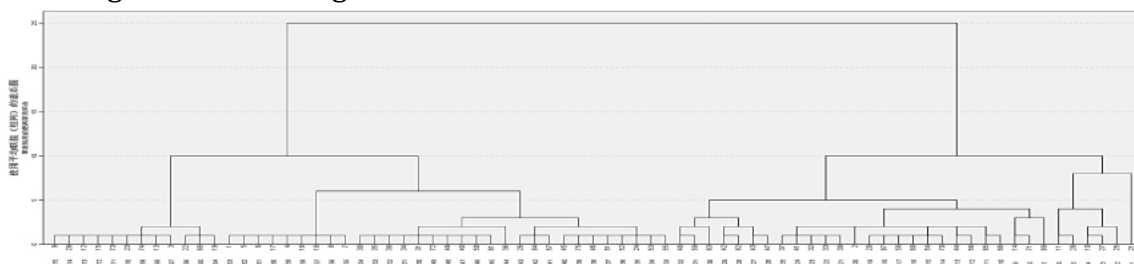


Figure 10. Cluster pedigree diagram

After cluster analysis, the classification results of unknown data are as follows:

Table 7. Unknown data classification table

Heritage Code	Classification of glass
A1	High potassium glass
A2	Lead barium glass
A3	Lead barium glass
A4	Lead barium glass
A5	High potassium glass
A6	High potassium glass
A7	High potassium glass
A8	Lead barium glass

The effective independent variables involved in this classification are SiO₂, K₂O, CaO, Fe₂O₃, PbO, BaO, P₂O₅ and SrO. The above are the valid variables related to glass classification obtained in the process of variable screening. Among them, if K₂O content is less than 0.445, glass can be divided into high potassium and non-high potassium; if BaO content is less than or equal to 6.985, glass can be divided into high barium and non-high barium. In this classification, the training set and the test set are divided into 7:3, and the Gini coefficient is used as the evaluation criterion for node splitting.

3.4. Excavation and Protection of Glass Relics

In this paper, "A Brief list of Important Unearthed Sites of ancient Chinese glass" is organized and drawn as a map.



Figure 11. The distribution of ancient glass

As can be seen from the figure, the unearthed glass relics in recent years are widely distributed, mainly in eastern China. Among them, Guangdong and Guangxi provinces are more densely distributed, and Hunan Province is the most. According to the time when the cultural relics were unearthed, the style of glass gradually evolved from monochrome glass beads at the beginning to ornaments and vessels with rich colors and various types of utensils. In this process, ancient people gradually learned to use the chemical composition of glass to control the color and style of glass objects. Ancient glass relics reappear in the world after a gap of nearly one thousand years and are vulnerable to wind and rain erosion. There are two main reasons for the damage of glass relics, one is physical damage, and the other is chemical erosion. Physical damage means that when glass relics are placed in the tomb, geological disasters or heavy rains occur in the area, the structure of the tomb changes, and the burial objects are broken or knocked.

And chemical erosion mainly refers to the weathering of glass. Glass in the process of placement will inevitably contact with water and gas, and then carry out a series of chemical reactions. Glass itself can be preserved for a very long time in an anhydrous environment, and its main component SiO_2 itself has high chemical stability. When the surface is in contact with water gas, a series of chemical reactions will occur and sensory changes will occur on the glass surface. In the study of this paper, we concluded that the weathering of glass is also related to the chemical composition inside the glass, so we made a reasonable guess that after the reaction of the glass surface with water vapor, the chemical properties will be active and then react with other components to further weathering. In the process of reaction, the alkalinity of the aqueous solution will also increase, and the caustic force will be enhanced. The whole network of the glass will be eroded by strong alkali, its oxygen bridge skeleton will be broken, the surface will be eroded, and the performance will appear rainbow, white spots, fog, and even sticky pieces.

In the transfer of cultural relics unearthed by adding filler or separate transfer, to avoid human error caused by the destruction of cultural relics. Control the temperature and humidity of the glass cultural relic storage space. Glass products are very sensitive to temperature, so try to avoid obvious temperature changes in the storage space to prevent cracking. It is better to control the relative humidity of the environment at 45% [5].

4. Conclusion

In view of the above research, we determined that SiO_2 , K_2O , CaO , Fe_2O_3 , PbO , BaO , P_2O_5 and SrO among the 14 variables provided in the data set may have a certain relationship with the classification of glass. In the further investigation, we determined that the contents of K_2O , SrO , BaO and PbO are directly related to the classification of glass. The basis for the classification of this batch of cultural relics glass is provided: the micro-level high-potassium glass is classified according to the content of main components, the lead-barium glass is classified according to the content of main components, and the macro-level glass is classified according to the weathering degree and color depth. The unknown data set is successfully classified by Kmeans and decision tree algorithm. Finally, reasonable countermeasures against glass weathering are put forward from both physical and chemical aspects, and effective suggestions are put forward for the excavation and protection of glass relics. As for the potential risks of the glass relics mentioned above, this paper believes that we should protect them from both physical and chemical aspects. In addition, try to prevent water vapor erosion in future storage of glass relics. Long-term water vapor erosion may cause chemical reactions, further damaging the original structure of the glass and losing its value.

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