Corrosion and Wear of Materials (2023)
Clausius Scientific Press, Canada

DOI: 10.23977/corwm.2023.020101
ISSN 2616-3098 Vol. 2 Num. 1

Research on Glass Weathering and Classification Problems in Ancient Times

Yiqi Luo*

School of Computer Science and Engineering, Southwest Minzu University, Chengdu, 610041, China

**Corresponding author*

Keywords: Entropy weight method; clustering method; BP neural network

Abstract: Glasses in ancient times tend to suffer from weathering when they are buried because of changes of the environment, which will affect the accurate judgment of its classification. This paper analyzes related data of ancient glass products in ancient times of China provided by 2022 National Mathematical Contest in Modeling for College Students and predicts their chemical composition contents before the weathering according to the statistical rules of chemical composition contents of the samples. A BP neural network model is built to analyze classification characteristics of high-potassium and lead barium glass. Besides, the entropy weight method and the clustering method are used together to subdivide two types of high-potassium and lead-barium glasses. It is hoped that this research can provide some reference for the composition analysis and category identification of ancient glass products.

1. Research Background

Class is a treasure favored by people living in ancient China. It is closely related to the ancient Silk Road and serves as a valuable material evidence of trade in the early days [1]. There were four Silk Roads in China from the north to the south. Specific routes for importing glassware in different periods were mainly determined by geographical and political situations at that time and the manufacturing techniques and patterns of glassware circulating on different routes were very different [2]. The large number of glassware unearthed in different periods of China not only reflect highly developed ancient craft technology but also show high historical and cultural value and artistic values [3]. Researches on glass weathering are done from two perspectives: one is from the viewpoint of chemical action while the other is from the perspective of microbial action [4]. This study only discusses the influence of chemical composition on glass weathering. The addition of different co-solvents in the process of glass refining by different processes resulted in different chemical compositions of the finished products. Ancient glass can be easily affected by burial conditions. During weathering, internal elements exchange a lot with environmental elements, resulting in changes in their composition ratio and archaeological workers' correct judgment of their categories, colors and patters [5, 6]. On the basis of this, this paper researches relevant data of a batch of ancient glasses through the entropy weight method, the clustering method and the BP neural network so as to explore weathering characteristics and classification rules of glasses in ancient times.

2. Research Hypothesis and Related Explanation

2.1. Research Hypothesis

It is assumed that the weathering of glass is only influenced by its chemical elements, without considering the influence of environmental factors.

It is assumed that the sum of the chemical composition of glass and that data between 85% and 105% in the subsequent calculation are valid data and there is no need to adjust the data amount.

It is assumed that the influence of other chemical composition contents on glass weathering other than the obtained data is not considered.

2.2. Research Explanation

Firstly, research data of this paper come from a batch of data of ancient Chinese glass products provided by the competition official in Question C of 2022 National Mathematical Contest in Modeling for College Students. Archaeologists have used professional technical means to give proportions of chemical components and types of glass of these cultural relic samples. That is to say, they are high potassium glass and lead barium glass respectively. After chemical components of the collected data are proportionally accumulated, if the data is between 85% and 100%, the data will be regarded as valid data. The undetected chemical component in the data is recorded as 0.

Second, symbols used in this paper are mainly listed in Table 1:

Table 1: Symbol explanation

Symbol	Explanation
n	Number of explanatory variables
β_0	Constant term
x_n	Explanatory variable
β_n ε	Regression coefficient of explanatory variable x_n (β_n is also known as the correlation factor coefficient) Random disturbance term
X	Forward matrix
Z	Normalized matrix
n	Evaluation object
m	Evaluation index
j	Index j, (j =1, 2, …, n)
i	Sample i, (i =1, 2, …, n)
P	Probability matrix
e_j	Information entropy of index j
d_j	Information utility value of index j
W_j	Entropy weight of index j

3. Research Process

3.1. Prediction of Pre-Weathering Chemical Composition

3.1.1. Data Processing

After data processing, two lines of data whose chemical composition of the glass is not between 85% and 105% are removed and tables are formed for statistical analysis based on glass types and whether its surface has weathering. The collated chart is shown in Table 2:

Table 2: Chemical composition content table

Chemical component	High potassium			Lead barium		
	Unweathered (%)	Weathered (%)	Rate of change	Unweathered (%)	Weathered (%)	Rate of change
SiO2	72.169	82.238	13.95%	54.660	26.438	-51.63%
Na2O	0.548	0.358	-34.76%	1.683	0.216	-87.15%
K2O	8.513	3.763	-55.80%	0.219	0.429	96.09%
CaO	5.154	2.209	-57.14%	1.320	2.847	115.58%
MgO	0.988	0.531	-46.23%	0.640	0.717	11.88%
Al2O3	5.558	4.430	-20.30%	4.456	3.305	-25.83%
Fe2O3	1.222	1.569	28.38%	0.737	0.817	10.92%
CuO	2.056	2.280	10.89%	1.432	1.959	36.84%
PbO	0.439	0.069	-84.34%	22.085	42.224	91.19%
BaO	0.483	0.294	-39.18%	9.002	10.643	18.24%
P2O5	0.709	1.428	101.34%	1.049	5.312	406.35%
SrO	0.027	0.029	6.48%	0.268	0.409	52.41%
SnO2	0.236	0.000	-100.00%	0.047	0.068	47.16%
SO2	0.122	0.000	-100.00%	0.159	1.267	696.15%

(1) “Weathered /%”in Table 2 includes all weathered points on all glass surfaces in the data, while “unweathered /%” includes all non-weathered glass surfaces and non-weathered points on weathered glass surfaces.

(2) The content of each chemical component is an arithmetic average calculated according to the type of glass and whether the surface is weathered. The average value is used to calculate the rate of change and make backward prediction.

Average value:

$$\bar{x} = \frac{x_1 + x_2 + \ldots x_n}{n} \tag{1}$$

For example, the data of high potassium glass not weathered is screened out to calculate the average value of each chemical composition.

Change rate =(average before and after weathering of each chemical component - average before weathering of each chemical component) ×100%.

(3) If the system reports errors, the change is negative (unweathered > weathered) and the weathered sample point is 0, the unweathered value = the mean unweathered value of the component - the mean weathered value of the component. It is then used to fill the data.

3.1.2. Backward Prediction

The change rate in Table 2 was used for backward calculation. After that, the sum of each sample is accumulated and scaled up or down to make the sum equal to 100% for the data that was accumulated and not within the effective range. Data whose sum is within the valid range remain the same.

Table 3 is the predicted chemical compositions of high potassium glass before weathering. It includes 8 sets of data:

Table 3: Predicted chemical compositions of high potassium glass before weathering

Chemical compositions	06 Part 1	06 Part 2	07	09	10	12	22	27
SiO2	55.48	47.29	81.29	83.39	84.92	82.75	42.80	81.37
Na2O	0.19	0.00	0.19	0.19	0.19	0.19	3.62	0.19
K2O	15.58	15.65	4.75	1.33	2.08	2.29	23.43	4.75
CaO	0.00	11.37	2.50	1.45	0.49	1.68	16.78	2.19
MgO	3.44	2.90	0.46	0.46	0.46	0.46	0.00	1.00
Al2O3	13.07	11.36	2.48	1.66	1.02	1.83	6.39	3.15
Fe2O3	1.74	4.24	0.13	0.25	0.20	0.23	1.85	0.16
CuO	2.12	1.77	2.92	1.40	0.76	1.49	3.53	1.39
PbO	1.19	2.01	0.37	0.37	0.37	0.37	0.37	0.37
BaO	2.12	1.44	0.19	0.19	0.19	0.19	0.19	0.19
P2O5	1.94	2.01	0.30	0.17	0.00	0.07	0.52	0.18
SrO	0.10	0.10	0.00	0.00	0.00	0.00	0.00	0.00
SnO2	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24
SO2	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
SUM	97.34	100.50	95.95	91.21	91.04	91.90	99.83	95.30

The same method is used to predict the composition of lead barium glass before weathering.

3.2. Analysis of Classification Rules of High Potassium Glass and Lead Barium Glass

3.2.1 Construction of BP Neural Network Model

BP neural network algorithm is used to analyze the unknown classification rules. BP neural network is a "backward" learning algorithm of multi-layer network, which consists of input layer, hidden layer and output layer [7]. The activation function of the input layer is an identity function whose output is the input.

If $y_1 = f(s_j) = s_j$

Then $x_{n0}^{(0)} = x_0$

In the first hidden layer, each nerve cell is fully connected with each neuron in the input layer, forming n1 × n0 connection weights and the connection matrix is W(1). Each nerve cell of the second hidden layer is completely connected with each nerve cell of the first hidden layer, forming n2 × n1 connection weight state, and the connection matrix is W(2). The hidden layer generally adopts S-type activation function, i.e

$$y_j = f(s_j) = \frac{1}{1+e^{-bs}} \tag{2}$$

Where, the output of the second hidden layer is

$$x^{(2)} = f\left(W^{(2)}x^{(1)}\right) \tag{3}$$

Supposed that the hidden layer has 2 layers, then each nerve cell of the output layer is completely connected with the nerve cell of the second hidden layer, which will formn3 ×n2. The connection matrix is W (3) and the activation function is the identity function. The output is

$$x^{(3)} = f\left(W^{(3)}x^{(2)}\right) \tag{4}$$

(4) The number of input layer units is 15 while that of the output layer units is 2.

(5) Methods to determine the number of hidden layers:

The research shows that the three-layer BP neural network with a hidden layer can achieve the best mapping effect of any closed interval continuous function approximation and any N-dimensional input space to m-dimensional output space. Therefore, the number of hidden layer is 1.

The number of hidden layer units can be determined according to formula (4):

$$j = \sqrt{n+m} + a \tag{5}$$

In the formula,

J—number of hidden layer units

n—number of input layer units

m—number of output layer units

a—a constant between 1 and 10

3.2.2. BP Neural Network Model Solution

Through forward signal propagation and back error propagation, SPSS can train existing data through neural network model to get a training model and then the model will be applied to predict the data set to get prediction results as shown in Figure 1:

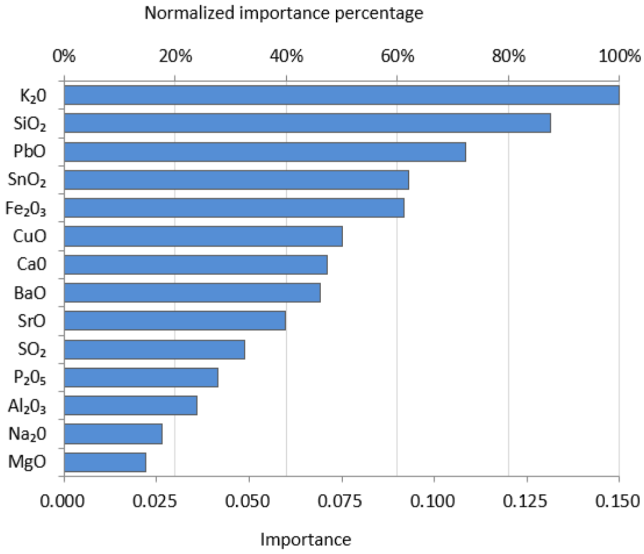

Figure 1: Normalized importance histogram

It can be seen from the figure above that the top five components exceeding 60%, namely K2O, SiO2, PbO, SnO2, Fe2O3, are the most important factors affecting the classification. Therefore, this paper focuses on analyzing these five components and compares their contents in high potassium and lead barium glass respectively. Finally, the first three components are selected. Relevant data analysis is shown in Table 4:

Table 4: Classification rules of two kinds of glass

Chemical component	High potassium			Lead barium		
	K2O	SiO2	PbO	K2O	SiO2	PbO
Average value	6.40	76.64	0.27	0.33	39.69	32.77
Standard deviation	5.31	14.47	0.51	1.11	18.68	15.66

As can be seen from the above table, classification rule of high potassium glass and lead barium glass are shown as follows:

(1) The average potassium oxide content of high potassium glass was higher, and the degree of dispersion between samples was greater;

(2) The average content of silicon dioxide in high potassium glass was higher than that in lead barium glass;

(3) The average lead oxide content of lead barium glass is higher, and the degree of dispersion between samples is greater;

3.3. Division of Glass Subclass Based on Entropy Weight Method and Clustering Analysis

3.3.1. Build Model through Entropy Weight Method

Silicon dioxide, the main ingredient in glass, can be mixed with other chemicals to change its properties, such as viscosity, thermal expansion and aging resistance [8]. The use of lead oxide in lead barium glass is mainly to reduce the melting temperature of glass, and the use barium oxide can also effectively reduce the melting temperature of glass [9].

According to the analysis of entropy weight method, potassium oxide, silicon dioxide and calcium oxide were selected as the important chemical components affecting the weathering of high potassium glass. Their weights were calculated and evaluated. This paper then use silicon dioxide, lead oxide and barium oxide as indicators for evaluation.

(1)Transform matrix forward (into extremely large index). When {xi} is an extremely small index, its forward formula is:

$$x_i\text{=max }\{x_i\}\text{-}x_i \tag{6}$$

With n objects to be evaluated and m evaluation indicators, the following matrix X is formed:

$$X=\begin{bmatrix} x_{11} & x_{12} & \cdots & x_{1m} \\ x_{21} & x_{22} & \cdots & x_{2m} \\ \vdots & \vdots & \ddots & \vdots \\ x_{n1} & x_{n2} & \cdots & x_{nm} \end{bmatrix} \tag{7}$$

The matrix composed of all indexes is then be standardizedand the matrix after the standardization is marked as Z:

$$Z_{ij}=\frac{x_{ij}}{\sqrt{\sum_{i=1}^{n} x_{ij}^2}} \tag{8}$$

Determine whether there is a negative number in the Z matrix. If there is a negative number, another normalization method will be done for X, and the formula is:

$$Z_{ij}=\frac{x_{ij}-min\{x_{1j},x_{2j},\cdots,x_{nj}\}}{max\{x_{1j},x_{2j},\cdots x_{nj}\}-min\{x_{1j},x_{2j},\cdots,x_{nj}\}} \tag{9}$$

(2)Supposed that there are n objects to be evaluated and m evaluation indexes, we can obtain the following standardized matrix Z:

$$\mathrm{Z_{ij}} = \begin{bmatrix} z_{11} & z_{12} & \cdots & z_{1m} \\ z_{21} & z_{22} & \cdots & z_{2m} \\ \vdots & \vdots & \ddots & \vdots \\ z_{n1} & z_{n2} & \cdots & z_{nm} \end{bmatrix} \tag{10}$$

Calculate the probability matrix P, where the formula for each element pij in P is as follows:

$$p_{ij} = \frac{z_{ij}}{\sum_{i=1}^{n} z_{ij}} \tag{11}$$

And

$$\sum_{i=1}^{n} p_{ij}=1 \tag{12}$$

(3) The information entropy of each index and the information utility are calculated. The entropy weight of each index will then be obtained through normalization.

Information entropy ofj index:

$$e_{ij} = -\frac{1}{\ln n}\sum_{i=1}^{n} p_{ij}\ln(p_{ij})\ \ (j = 1,2,\cdots,m) \tag{13}$$

Information utility value of indexj:

$$d_j = 1 - e_j \tag{14}$$

Normalize them to get the entropy weight of each index:

$$W_j = \frac{d_j}{\sum_{j=1}^{m} d_j}(j = 1,2,\cdots,m) \tag{15}$$

3.3.2. Establishment of Clustering Analysis Model Based on Entropy Weight

Matlab is used to find solutions through entropy weight method and the results are as Table 5 and Table 6:

Table 5: Weight of main chemical composition of high potassium glass

Chemical composition	potassium oxide	silicon dioxide	calcium oxide
Weight	0.4949	0.0195	0.4856

Table 6: Weight of main chemical composition of lead barium glass

Chemical composition	silicon dioxide	lead oxide	barium oxide
Weight	0.2280	0.2328	0.5392

According to the entropy value, potassium oxide accounted for the highest weight among the main chemical components of high potassium glass, and barium oxide accounted for the highest weight among the main chemical components of lead barium glass.

Therefore, this paper decides to use the clustering analysis method for subclass division of high potassium glass with chemical composition contents of potassium oxideK2O. Chemical composition contents of barium oxide BaO are then used for subclass division of lead barium glass [10,11]. Each type of glass is divided into three categories and their corresponding chemical contents are respectively shown as high, medium and low. The specific data is shown in Table 7:

Table 7: Subdivision table of two types of glass

Glass types	Chemical composition content (potassium oxide/barium oxide)		
	High	Middle	Low
High potassium glass number	03 part 2, 5 13, 14, 22	1, 03 part 1 4, 16, 06 part 1 06 part 2	18, 21, 7 10, 9 12, 27
lead barium glass number	08 severe weathering 26 26 severe weathering	20 24 11 50 56 57	30 part 1, 30 part 2 31, 32, 33, 35, 37 45, 46, 47, 55 23 unweathered, 25 unweathered 28 unweathered, 29 unweathered 42 unweathered1, 42unweathered2 44 unweathered, 49 unweathered 50 unweathered, 53 unweathered 8, 2, 19, 34 36, 38, 39, 40, 41 43 part 1, 43 part 2 48, 49, 51 part 1 51 part 2, 52, 54 54 severe weathering, 58

As can be seen from the table, high potassium glass can be classified into high potassium, medium potassium and low potassium according to chemical composition contents of K2O, and the numbers of sub-classes are 5, 6 and 7 respectively.

Similarly, lead barium glass can be also divided into high barium, medium barium and low barium according to the chemical composition content of BaO and the number of sub-classes is 3, 6 and 40.

3.3.3. Clustering Rationality Analysis

Independent-samples T test and one-way analysis of variance is used to analyze the rationality of the above classification. High potassium glass has 18 samples while lead barium glass has 49 samples. Due to the difference in sample size between the two types of glass, it is not appropriate to adopt the same test method for small sample and large sample. Therefore, it is appropriate to use independent-samples T test for subclass high potassium glass, and one-way analysis of variance for subclass lead barium glass.

t statistical magnitude of independent-samples T test is:

$$t=\frac{\overline{x}-\overline{y}}{S_w\sqrt{\frac{1}{m}-\frac{1}{n}}}\sim t(m+n-2) \tag{16}$$

Among which,

$$S_w=\frac{1}{m+n+1}\left[(m-1)S_1^2+(n-1)S_2^2\right] \tag{17}$$

α=0.05

$\bar{x}$ is the first sample mean, $\bar{y}$ is the second sample mean, mis the first sample size, nis the second sample size, S_1^2 is the first sample variance, S_2^2 is the second sample variance.

Since there are three sets of data, SPSS is used to conduct independent-sample T test for pairwise comparison.

Independent-samples T test for low potassium oxide content and medium potassium oxide content. The results are shown in Table 8:

Table 8: Independent-samples T test for low and medium potassium oxide

potassium oxide		Levin's test for equality of variance		Mean equality t test			
		F	significance	t	DOF	Sig.(two-tailed test)	Mean difference
	Equi-variance assumed	10.316	.008	10.861	11	.000	7.75429
	Equi-variance not assumed			10.078	5.528	.000	7.75429

Independent-samples T test for low and medium potassium oxide content concentration. The results are shown in Table 9:

Table 9: Independent-samples T test for low and high potassium oxide concentration

potassium oxide		Levin's test for equality of variance		Mean equality t test			
		F	significance	t	DOF	Sig.(two-tailed test)	Mean difference
	Equi-variance assumed	1.559	.243	-4.413	9	.002	-4.31000
	Equi-variance not assumed			-4.570	8.791	.001	-4.31000

The two comparative analyses aimed to compare the low and medium potassium oxide content respectively. As can be seen from the above table, the variance significance ($t>0.05$) of both T-tests failed, but the mean significance ($Sig<0.05$) passed. In summary, three subclasses of high potassium glass had significant differences in data mean value and they are reasonably classified.

Because continuous data of multiple groups need to be compared and the homogeneity test result of variance is homogeneity. One-way analysis of variance (ANOVA) test is used for sub-categories of lead barium glass and the test results are shown in Table 10:

Table 10: One-way analysis of variance

Barium oxide	Quadratic sum	Degree of freedom	Mean square	F	Significance
Between groups	2390.589	2	1195.294	94.314	.000
Inside the group	582.987	46	12.674		
Sum	2973.575	48			

According to the above analysis, $p<0.05$ was obtained after referring to Bonfreni and ANOVA data. Therefore, through the test, there were significant differences among the three subcategories of lead barium glass and the classification was reasonable.

3.3.4. Sensitivity Analysis -- BP Neural Network Prediction

In sensitivity analysis, the dependent variable is changed into three categories of glass types after classification: high, medium and low according to the subcategories of glass. All chemical components are used as the independent variable. The data are then put into BP neural network for training and testing.

The sample is the smallest sample for "distance from the case to its classification clustering center", which is very close to the central value of its own classification, so it is representative. The sample of high potassium glass is glass number 22 and the sample of lead barium glass is glass number 34. Sensitivity analyses for both glass classifications float SiO2 up or down by 10% with a step size of 0.1 and other components unchanged.

For example, number 22 is selected in all samples of original high potassium and its clustering classification is category 3. The silicon dioxide component value in the sample is changed while other components remain unchanged. 119 virtual samples are then generated and the silicon dioxide value of these virtual samples increase. BP neural network prediction is used to analyze whether the virtual sample will maintain the original classification (category 3). The sensitivity analysis is shown as Figure 2:

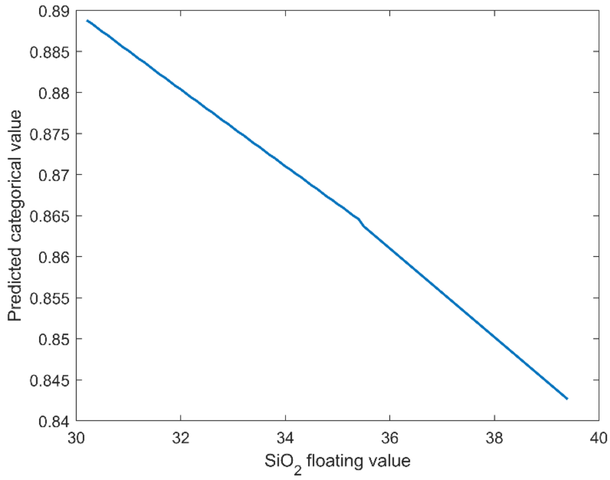

Figure 2: Sensitivity of silicon dioxide change to the classification of high potassium

According to Figure 3, a small change in silicon dioxide content can lead to a large change in the quantitative data of the classification. Therefore, silicon dioxide is the sensitive factor affecting the classification of High potassium glass subclass.

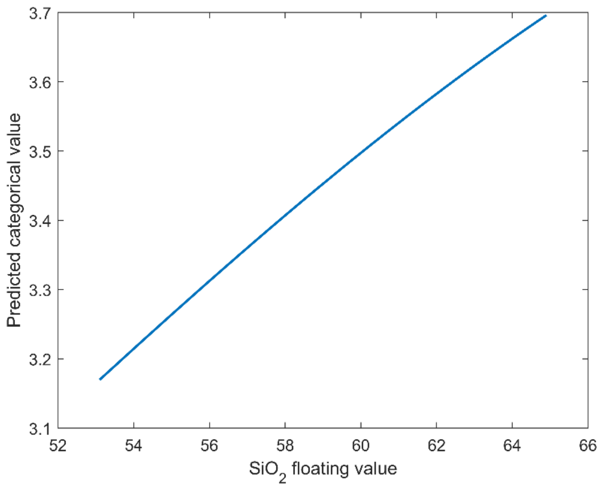

Figure 3: Sensitivity of silicon dioxide change to the classification of lead barium

As shown in the figure, a small change in silicon dioxide contents will lead to a large change in the quantitative data of the classification. Therefore, silicon dioxide is a sensitive factor affecting the subdivision of lead barium glass.

4. Summary and Reflection

This paper aims to explore the statistical rule of chemical composition content of ancient glass weathering and predict its chemical composition content before weathering through data analysis and modeling. Classification characteristics of high potassium and lead barium glass are also analyzed. Traditional ancient glass products are divided into subcategories according to their compositions difference, which can provide referential models and methods for compositive analysis, classification and differentiation of ancient glass products in our country. In the early clustering stage, composition characteristics of high potassium and lead barium glass are analyzed by BP neural network and then the influence of important components of the two kinds of glass is objectively determined by entropy weight method. Finally, the most influential component is used as the basis for subclass classification. After clustering process, the rationality of the category is analyzed and the sensitivity of the classification model is also analyzed. This means that the classification model is effective and meaningful.

Among researches of glass weathering, one is done from the viewpoint of chemical action while the other is from the perspective of microbial action. This study researches weathering only from the perspective of chemical composition, which indicates that there is still some limitations. Due to the limitation of data resources, it is impossible to compare weathering degree and chemical composition at multiple points on the same glass cultural relic. However, in fact, chemical compositions of different weathering sites of different cultural relics may be significantly different under the influence of preservation environment, year, technology and other factors. In this study, multiple cultural relics and weathering points are selected for comparison. Its accuracy remains to be improved.

References

[1] Yang J., (2016). Western Cultural Exchange Viewed from Foreign Glass Products on Silk Road. National Art, (01): 88-93.

[2] Chen S. Y., Hou Z. L., (2019) Analysis on Ancient Silk Road and Ancient Chinese Glass. Exhibition of China Nationalities, (05): 87-88.

[3] Chen S. Y., (2019) Origin and Development of Ancient Chinese Glasses. Cultural Relic Identification and Appreciation, No. 151 (04): 44-45.

[4] Wang C. Y., Tao, Y., (2003) Weathering of Silicate Glass. Journal of the Silicate, (01): 78-85.

[5] Lu J. J., (2010) Classification Model of Ancient Glass based on Integrated Feature Selection and Random Forest. Journal of the Chinese Society of Ceramics, 51 (04): 1060-1065.

[6] Yin Y. L., (2023) L. Composition Analysis of Ancient Glass Products by Association Prediction. Contemporary Chemical Research, No. 126 (01): 122-126.

[7] Song A. P., Gong H. Y., [2022-09-17] Research on the Law of Ammunition Heat Transfer Based on BP Neural Network. Journal of Missile, Arrow and Guidance: 1-4.

[8] Zhou J., (2021). Connection and Unique Wisdom of Chu Glass Art and Foreign Crafts. Journal of Suzhou Arts and Crafts Vocational and Technical College, (01): 6-11.

[9] Zhou J., (2021). A General View of the Artistic Obsession of Lead Barium Glass in China. Grand View of Art, (03): 184-186.

[10] Ouyang J., Huang C. Y., Li S., Li J., Peng Z., et al. [2022-09-18] Construction of Flavor Wheel and Flavor Classification Model of Golden Tea and Green Tea. Food and Fermentation Industry: 1-10.

[11] Zhang C. H., Li C. B., Wu J., (2022). Study on Subclass Classification of Mountain Grassland in China based on Comprehensive Sequential Classification of Grassland. Acta Prataculturae Sinica, 31 (03): 16-25.