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A study of the problem of compositional analysis of ancient glassware based on grey models

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Abstract: *In ancient times, glass was a valuable object of trade between China and the West, with potassium glass and lead-barium glass being common. In order to classify and identify ancient glass objects, this paper establishes a relevant classification model based on the chemical composition of glass, which is of some significance for the classification and analysis of glass. In this paper, the frequency distribution of each component is plotted as non-standard normal distribution, and then Spearman correlation coefficient is selected to describe its correlation, and it is found that SiO_2 has a more active relationship with other components, so it is chosen as the reference column for grey correlation analysis, and it is concluded that SiO_2 is closely related to the flux component of its glass type.*

Keywords: *Glass products, Grey correlation, Classification study*

1. Introduction

From the early days of trade between China and the West, when glass was made into ornaments and flowed into China, our glass making techniques have become more and more abundant.[1] In the making of glass, auxiliary solvents such as grass ash, natural gas bubble soda, saltpeter and lead ore were added, and limestone was used as a stabiliser for quartz sand. In recent years research in glass has become more and more enriched with the excavation of ancient glass from all over the world.

Wen[2] et al. used binary statistical analysis to classify the glass system of ancient glass beads and to describe the geographical distribution; Qin[3] et al. found that the presence of barium carbonate ore was the most fundamental factor in the genesis of lead-barium glass through a series of simulations; Yuan[4] et al. used X-ray fluorescence spectroscopy for non-destructive analysis of ancient glass to identify glass classes; Hu[5] et al. analysed the elements of ancient glass by LA-ICP-MS and found that the calibration strategy of the glass standard NIST 610 as a standard combined with the matrix normalisation method could accurately reflect the compositional composition in different types of ancient glass materials; Rossano[6] et al. analysed the production process of ancient glass colours by analysing the Mn-Fe elements of glass.

Previous studies have not analysed the composition of ancient glass in detail. This paper analyses the classification of glass and the compositional relationships based on the differences between high potassium glass and lead-barium glass co-solvent elements. By classifying the chemical composition of ancient glass samples excavated in Chongqing and Sichuan, China, and analysing the correlation between the chemical components and the correlation between the elements of different types of glass, we can improve the efficiency of the classification of ancient glass products and provide reference significance for the production of glass products and subsequent research.

2. Linear Discriminant Analysis & Gray Correlation Analysis

2.1 Linear discriminant analysis

The main idea of linear discriminant analysis(LDA) [7], as a supervised learning method of

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dimensionality reduction considering category output, is to project the data in low dimensions, and the projected data satisfies that the similar data points are as close as possible and the category centers of dissimilar data points are as large as possible. Its main optimization objectives are.

$$\arg\max J(w) = \frac{w^T(\mu_0-\mu_1)(\mu_0-\mu_1)^T w}{w^T(\Sigma_0+\Sigma_1)w}$$

where μ_j is the mean vector of the jth class of samples, Σ_j is the covariance matrix of the jth class of samples, w is the projection direction weight.

$$\Sigma_j = \sum_{x\in X_j}(x-\mu_j)(x-\mu_j)^T, \mu_j = \frac{1}{y_j}\sum_{x\in X_j} x$$

2.2 Gray correlation analysis

Gray correlation analysis [8] measures the degree of association between factors based on the degree of similarity or dissimilarity of developmental dynamics between factors. For complex objective things, this method can quantify the importance of the influencing factors of complex phenomena. Its general steps are as follows.

Step1 Determine the analysis series

The analysis series usually includes the reference series and the comparison series, the reference series is the data series that reflects the characteristics of the system behavior, and the comparison series is the data series used to compare with the reference series [1].

Step2 carries out the dimensionless processing of the series

Dimensionless processing refers to converting data of different dimensions to the same dimension, so that the data have the same reference meaning and facilitate data convergence.

Step3 Calculation of the number of links

$$\zeta_i(k) = \frac{\min\limits_i \min\limits_k |X_0(k)-|X_i(k)| + \rho \max\limits_i \max\limits_k |X_0(k)-|X_i(k)|}{|X_0(k)-|X_i(k)| + \rho \max\limits_i \max\limits_k |X_0(k)-|X_i(k)|}$$

Resolution factor ρ is a value in the range of [0,1], which reflects the magnitude of the resolving power and is generally taken as 0.5.

Step4 Calculate the correlation degree and correlation ranking

The correlation coefficient reflects the degree of correlation between the two, but since it has a value at each moment, the information is too scattered to facilitate a holistic comparison. Therefore, the correlation coefficients at each moment are averaged as a quantitative representation of the degree of correlation between the comparison series and the reference series, and then ranked according to the magnitude of the correlation values, so that they can be easily compared in a holistic manner. The formula for the degree of correlation is as follows.

$$r_i = \frac{1}{N}\sum_{k=1}^{N}\xi_i(k)$$

3. Classification of glass types

As glass products add different cosolvent, their main chemical composition will also vary. Among them, potassium glass uses a substance with high potassium content as a cosolvent, with a high content of potassium oxide (K2O); lead-barium glass uses lead ore as a cosolvent, resulting in a high content of lead oxide (PbO) and barium oxide (BaO). In this paper, the K2O, PbO and BaO classification criteria X_i are selected, and the glass type is the classification variable y_0. A linear discriminant classification model is established as follows.

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$$y_0 = \begin{cases} \text{High potassium glass} & ,\omega^T x \geq 0 \\ \text{Lead} - \text{barium glass} & ,\omega^T x < 0 \end{cases}$$

By solving using python, in 2D-LDA, the partition weight vector w = [0.2412576, -0.14086467]. In 3D-LDA, the partitioning weight vector w = [0.27223459, -0.14858161, -0.15872573].

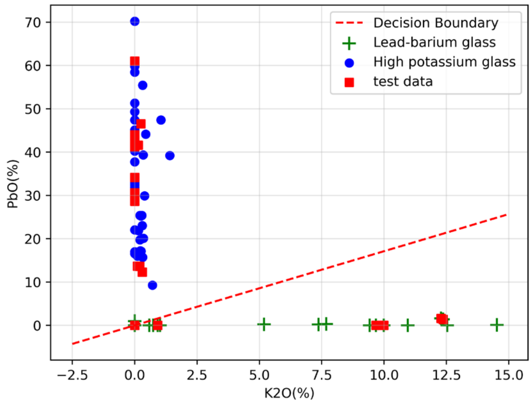

Figure 1: 2D-LDA

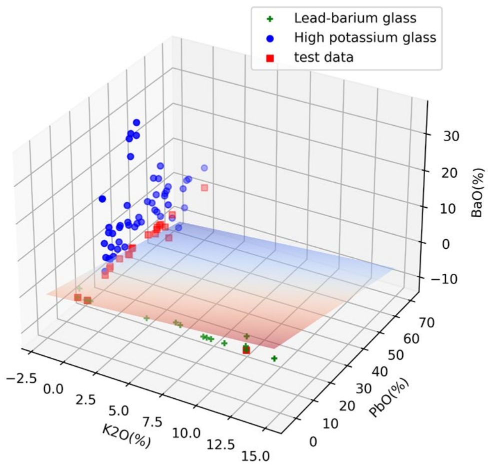

Figure 2: 3D-LDA

As shown in figures 1 and 2, the glass is perfectly divided into 2 categories. By testing the model, it was found to be 100% accurate.

4. Correlation and variation analysis of the chemical composition of glass

The chemical components were first tested for normality and the frequency distribution histograms are shown in Figures 3.

From the above figure, it can be found that all the chemical components do not show a standard normal distribution, so this paper uses *Spearman's* correlation coefficient method[9] for correlation analysis

$$r = 1 - \frac{6\sum (x_i - y_i)^2}{n(n^2 - 1)}$$

where n is the sample size and $r \in [-1,1]$

By using Python to solve and plot the heat diagrams for the different glass types are shown in Figures 4 and 5.

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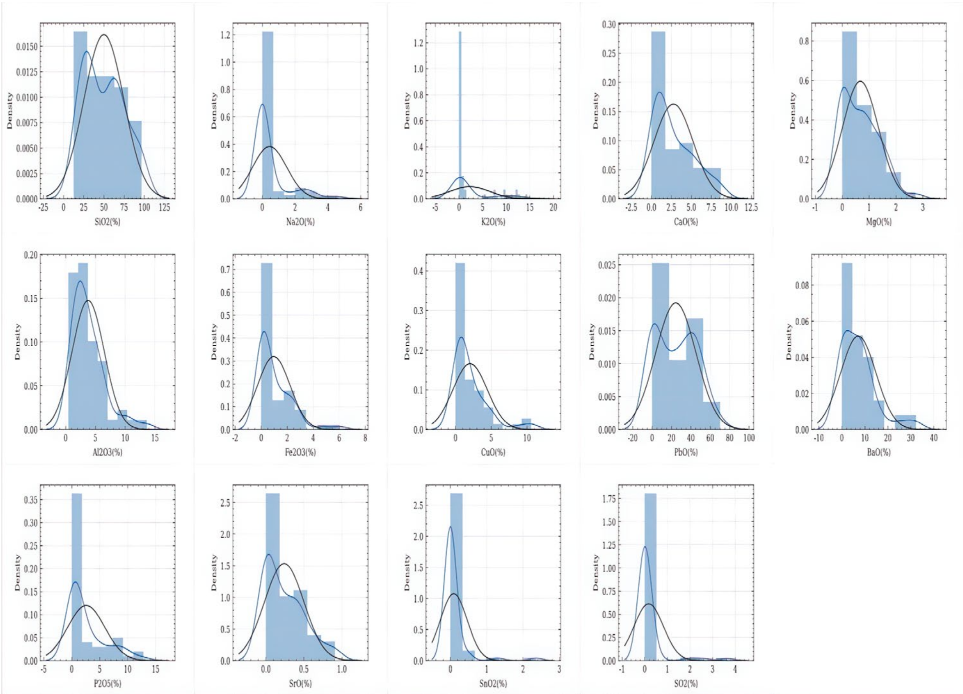

Figure 3: Histogram of frequency distribution of each chemical component

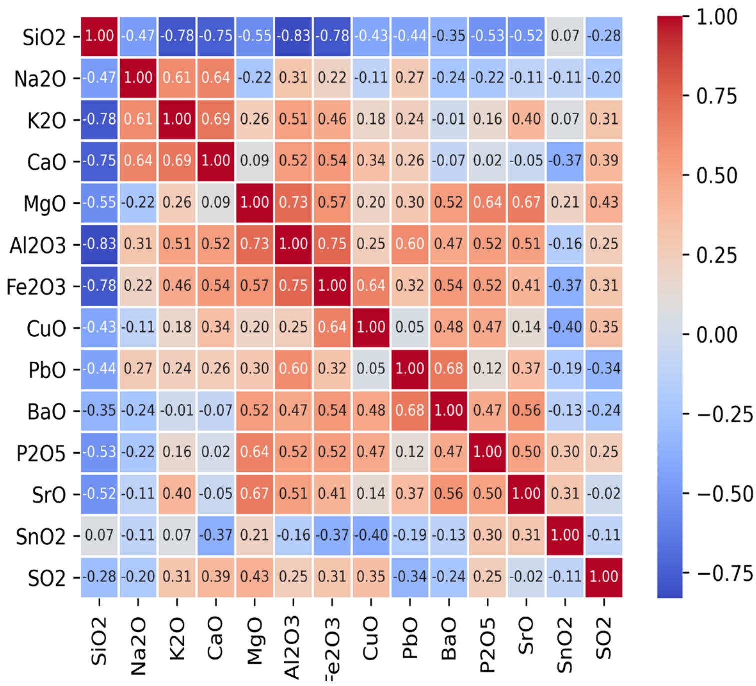

Figure 4: Thermal diagram of the chemical composition dependence of high potassium glass

The closer the correlation coefficient is to 1 the higher the correlation between the two variables. It can be found that among the high potassium glasses, Fe_2O_3 and Al_2O_3 have the strongest positive correlation (0.75) and Al_2O_3 and SiO_2 have the strongest negative correlation (-0.83). Apart from this, SiO2 is negatively correlated with all other chemical compositions and MgO is positively correlated with all other chemical compositions.

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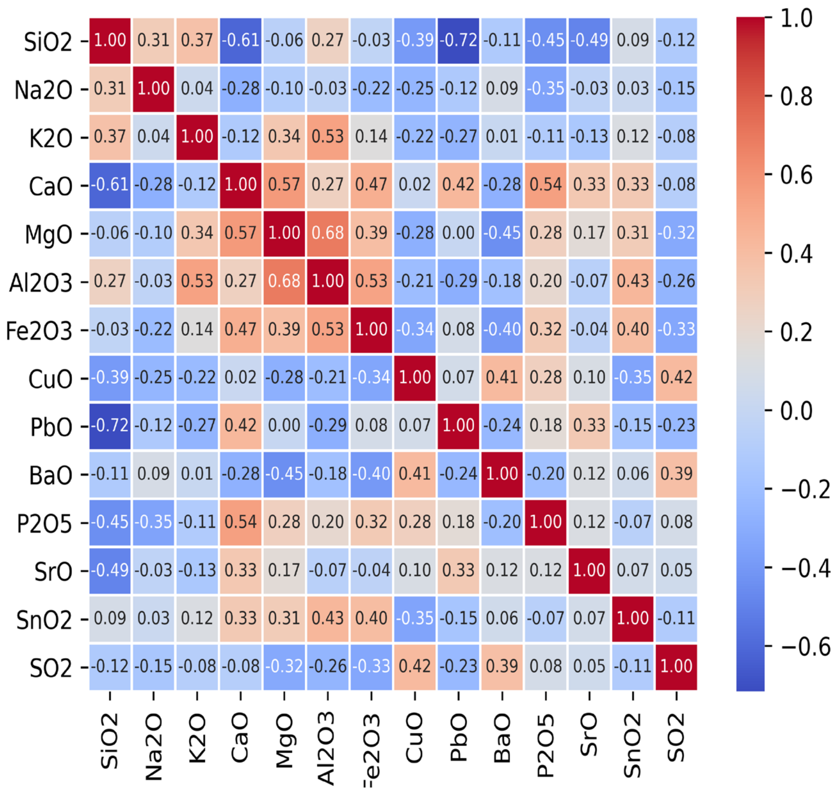

Figure 5: Thermogram of chemical composition correlation for lead barium glass

As can be seen from the graph, the overall correlation of the elements in lead-barium glass is not obvious, with MgO having the highest positive correlation with Al_2O_3 (0.68) and SiO_2 having the highest negative correlation with PbO (-0.72). It remains the case that SiO_2 shows a negative correlation with each of the other components.

In summary, the degree of correlation between the components is inconsistent as the production process differs between the glass types (different fluxes added). As the SiO2 composition of both the high potassium glass and the lead-barium glass show a negative correlation with the other chemical components, SiO2 was chosen as the reference sequence for analysis in this article.

5. Results

5.1 The establishment of grey model

Firstly, SiO_2 with the most significant correlation was selected as the parent sequence X_0 and the rest of the components as the comparison sequence X_i . The correlation coefficients between them were calculated directly without dimensionless treatment because the magnitudes were the same. $\zeta_i(k)$

$$\zeta_i(k)=\frac{\min_i\min_k|X_0(k)-|X_i(k)|+\rho\max_i\max_k|X_0(k)-|X_i(k)|}{|X_0(k)-|X_i(k)|+\rho\max_i\max_k|X_0(k)-|X_i(k)|}$$

5.2 Analysis of experimental results

The results of the correlations calculated through SPSS are shown in Table 1 below. As shown in the results in Table 1, in the high potassium glasses, SiO_2 showed high correlations with all components, all above 0.7, with the highest correlations with K_2O and Al_2O_3 and CaO.

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Table 1: High potassium grey correlation results

Evaluation items	Relevance	Ranking
Potassium oxide (K_2O)	0.82	1
Aluminium oxide (Al_2O_3)	0.806	2
Calcium oxide (CaO)	0.798	3
Copper oxide (CuO)	0.783	4
Iron oxide (Fe_2O_3)	0.779	5
Phosphorus pentoxide (P_2O_5)	0.776	6
Magnesium oxide (MgO)	0.774	7
Sodium oxide (Na_2O)	0.772	8
Barium oxide (BaO)	0.771	9
Lead oxide (PbO)	0.77	10
Tin oxide (SnO_2)	0.769	11
Sulphur dioxide (SO_2)	0.769	12
Strontium oxide (SrO)	0.768	13

As shown in Table 2, the correlations between SiO_2 and each of the components in lead-barium glass are moderate, all around 0.5, with the highest correlations with PbO and BaO.

Table 2: Lead and barium grey correlation results

Evaluation items	Relevance	Ranking
Lead oxide (PbO)	0.622	1
Barium oxide (BaO)	0.585	2
Phosphorus pentoxide (P_2O_5)	0.559	3
Aluminium oxide (Al_2O_3)	0.551	4
Calcium oxide (CaO)	0.546	5
Copper oxide (CuO)	0.546	6
Magnesium oxide (MgO)	0.53	7
Iron oxide (Fe_2O_3)	0.53	8
Sodium oxide (Na_2O)	0.53	9
Strontium oxide (SrO)	0.529	10
Potassium oxide (K_2O)	0.527	11
Tin oxide (SnO_2)	0.526	12
Sulphur dioxide (SO_2)	0.522	13

In summary, the various types of glass show a high correlation between the SiO_2 composition and the corresponding flux composition due to the inconsistency of the fluxes added during production, as appropriate for each type of glass.

6. Conclusions

In this paper, the whole process of glass product classification is described accurately and cleverly to a certain extent. A frequency distribution graph is made for each component, which is approximately normally distributed, and then the *Spearman* correlation coefficient is chosen to describe its correlation, and it is found that SiO2 has a more active relationship with other components, so it is chosen as the reference column for grey correlation analysis, and it is concluded that SiO2 is closely related to the co-solvent component of its glass type. Based on the analysis of data of ancient glass products, this paper innovatively constructs a basic model for the classification of glass products, which improves the efficiency of the classification of glass products and provides certain reference significance for the planning and selection of industrial production process paths.

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