Study on Chemical Composition Analysis and Methods of Ancient Glass Relics

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Abstract. In this paper, the relationship between the surface weathering of glass artifacts and the type, decoration, and color of glass was visualized by using a columnar table analysis[1], and the relationship between the three factors on the surface weathering was tested separately for significance by using a chi-square test; in addition, a multi-factor ANOVA was used to analyze whether the three factors of the type, decoration, and color of glass and their interaction on the surface weathering of glass artifacts had The significant relationships were analyzed by multivariate ANOVA. Then, the relative contributions of different types of glass to the prediction accuracy of the model were ranked by importance according to the proportion of chemical components before and after weathering at each sample point through random forest, and the chemical components were selected according to the importance ranking, and after removing most of the unimportant chemical components, the final retained chemical components were used to construct the final random forest regression model to obtain the laws of their classification, and finally the corresponding The results were obtained. The chemical components such as calcium oxide, copper oxide, iron oxide, and nitrogen oxide were drawn for visual analysis according to their importance, and we compared the derived results with the known literature and found that they were consistent with the results classified by the known literature.

Keywords: Analysis of Columnar Tables, Multi-factor analysis of variance (ANOVA), Random Forest algorithms, Ancient Glassware.

1. Introduction

Ancient glass [2] is highly susceptible to weathering by the burial environment. During the weathering process, a large number of internal elements are exchanged with environmental elements, resulting in changes in its composition ratio, which affects the correct judgment of its category.

In this paper, we collected data related to glass products, classified them into high potassium glass and lead-barium glass [3], and conducted modeling analysis based on their related data. The weathering of the glass surface is analyzed in terms of type, decoration and color, respectively, and the classification rules of high potassium glass and lead-barium glass are found out, and the division methods and results are given, and finally the results are analyzed in terms of reasonableness and sensitivity [4].

2. Introduction of the model

2.1. Columnar Table Analysis Model

The contingency table analysis can grasp the data distribution of multiple variables under different values, so as to further analyze the mutual influence and relationship between variables; Chi-square test can help us better judge whether there is a correlation between variables.

2.2. Multi-factor analysis of variance model

ANOVA is a method to test whether there is a significant difference between the means of 2 or more samples. In this paper, a multi-factor ANOVA model is developed to investigate whether the effects of glass type, decoration, and color on the surface weathering of glass artifacts are significant

and to analyze whether the interactions of three different factors have significant effects on glass artifacts.

2.3. Random Forest Model

From the 69 samples in the data we obtained, and the 14 chemical components in the correspondi ng samples, we want to find out the classification pattern in them, and we can use the easy-to-implement random forest model.

We use whether the samples are weathered or not and the corresponding 14 chemical component s as variables v. We apply the random forest model for training, test the OOB error of each sample, and obtain the importance ranking of the sample variables.

$$\mathbf{MDA(v)} = \frac{\mathbf{1}}{\mathbf{ntree}} \sum_{\mathbf{t}} (\mathbf{errOOB_t} - \mathbf{errOOB_t}') \tag{1}$$

$$\mathbf{G(t)} = \mathbf{1} - \sum_{\mathbf{K=1}}^{\mathbf{Q}} \mathbf{p^2(k/t)} \tag{2}$$

3. Results

3.1. The results of the contingency table model

In this paper, the relationship between the surface weathering of glass relics and the glass types, patterns and colors is studied by using the method of analysis of the list and Chi-square test. The collected data of glass cultural relics are classified according to the three attributes of type, ornamentation and color [5], and then the sequential contingency table, sequential contingency table and sequential contingency table can be obtained respectively. In order to facilitate viewing, the sequential contingency table is properly combined and the following table is obtained.

Table 1. Glass relic surface weathering and decoration, type contingency table

		decoration				type		
		A	B	C	total	Lead barium	High potassium	total
Surface weathering	weathering	11	6	17	34	28	6	34
	unweathered	11	0	13	24	12	12	24
total		22	6	30	58	40	18	58

As can be seen from Table 1, there are three types of glass decoration, including 6 Type B decoration and 17 type C decoration, indicating that C decoration is relatively easy to weather. There are two types of glass, including 28 lead-barium glass weathering and 6 high-potassium glass weathering, indicating that lead-barium glass weathering is easier.

Table 2. Glass relic surface weathering and color contingency table

		color								
		Black	Blue-green	Green	Light blue	Light green	Dark blue	Dark green	Purple	total
Surface weathering	weathering	2	9	0	12	1	0	4	2	30
	unweathered	0	6	1	8	2	2	3	2	24
total		2	15	1	20	3	2	7	4	54

As there are too many colors of glass, we process the data of colors separately. As can be seen from Table 2, there are 8 colors of glass. In weathering and unweathering, light blue is the largest, and green is the smallest.

Next, we determine whether there is a significant difference according to the Chi-square test results in Table 3.

Table 3. Chi-square test of decoration, type, color and surface weathering of glass

	decoration		type		color	
	value	Progressive significance (bilateral)	value	Progressive significance (bilateral)	value	Progressive significance (bilateral)
Pearson chi-square	4.957a	.084	6.880 a	.009	6.287 a	.507
Likelihood ratio	7.120	.028	6.889	.009	8.156	.319
Linear correlation	.137	.712	6.762	.009	.873	.350
Number of valid cases	58		58		54	

As can be seen from the Table 3, the surface weathering of glass and decoration, type and color is 0.084, 0.009 and 0.507, respectively. Then, the P value of decoration and type is less than 0.1, which is consistent with the inferred results of the contingency table.

3.2. The results of multivariate analysis of variance

Table 4. Multi-factor ANOVA for weathering of glass artifact surfaces

Source	Class III sum of squares	Degree of freedom	Mean Square	F	Significance
Modified model	7.933[a]	15	0.529	3.722	0.001
intercept distance	40.333	1	40.333	283.827	0.000
Type	1.487	1	1.487	10.462	0.003
Ornamentation	3.549	2	1.775	12.488	0.000
Color	1.489	7	0.213	1.497	0.198
Ornament * Color	0.091	1	0.091	0.637	0.430
Ornament * Type	0.000	1	0.000	0.000	1.000
Color * Type	0.387	3	0.129	0.908	.446
Error	5.400	38	0.142	0	0
Total	126.000	54	0	0	0
Total after correction	13.333	53	0	0	0

From Table 4 can be seen that the p-values of type and decoration are 0.003 and 0, respectively, which are significantly related to whether weathering, while the p-value of color is 0.198, which has no significant effect; the p-values of decoration, type, and color are all greater than 0.1 without significant effect under the two effects. That is, whether the surface of glass artifacts is weathered or not is significantly related to glass type and decoration, and there is no significant relationship with color.

The results were consistent through the chi-square test of the column table and analysis of variance.

Significant correlation between surface weathering of artifacts and glass ornamentation, with Class C ornamentation being more susceptible to weathering.

The surface weathering of artifacts correlates significantly with the type of glass, and lead-barium glass is more prone to weathering.

3.3. The results of Random Forest model

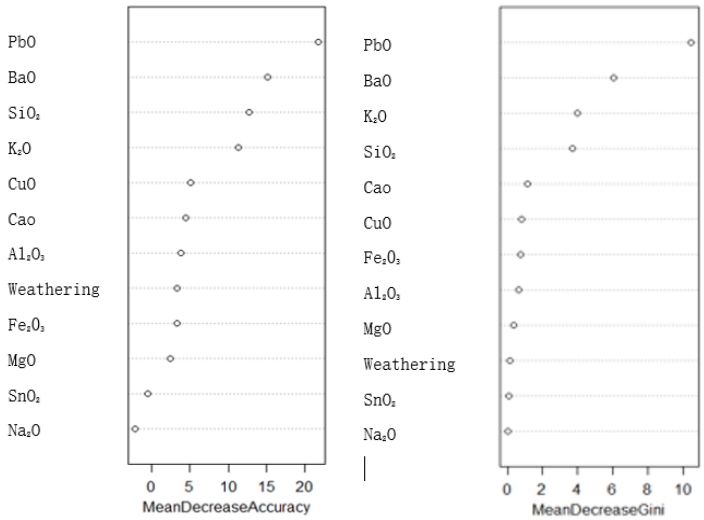

Figure 1. Random Forest ranking of importance for all chemical components

This results in the following graphs Mean Decrease Accuracy and Mean Decrease Ginidou, then both graphs are used to measure the importance of the sample variables, and the higher the value the higher the importance. It can be seen that the first four importance of Mean Decrease Accuracy and Mean Decrease Ginidou are consistent, so we took the four most important variables for validation and found that lead oxide, barium oxide, silica, and potassium oxide are significant [6].

Based on the error profile plot below, we used a cross-validation method where we selected four chemical components as significant variables and selected 80% of the samples from the sample set as a training set and the remaining 20% as a test set by a simple sampling method, and generated a decision tree with the sample set obtained from the sampling and estimated the prediction accuracy for the remaining 20% of the samples.

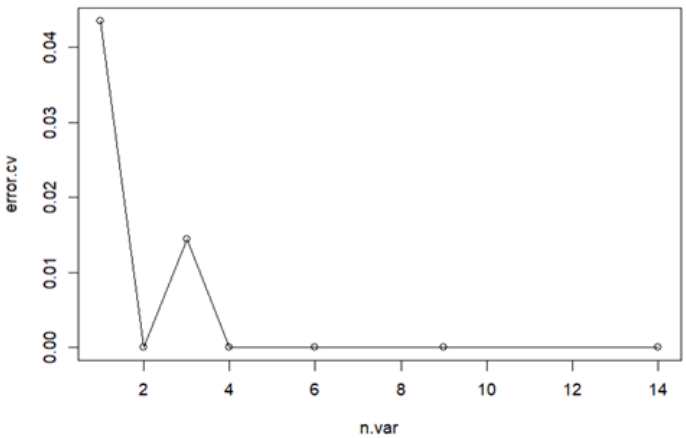

Figure 2. Error Curve Chart

In each node generated: 4 chemical components are randomly selected without repetition, and then these 4 chemical components are used to divide the sample set separately to find the best division feature, repeating the steps a total of u times, and u is the number of decision trees in the random forest. By dividing the training set, test set, and multiple runs, we found that the prediction accuracy obtained by cross-validation was 100% correct, so we finally selected four significant variables, namely, lead oxide, barium oxide, silica, and potassium oxide, and also conducted significant analysis based on these four significant variables.

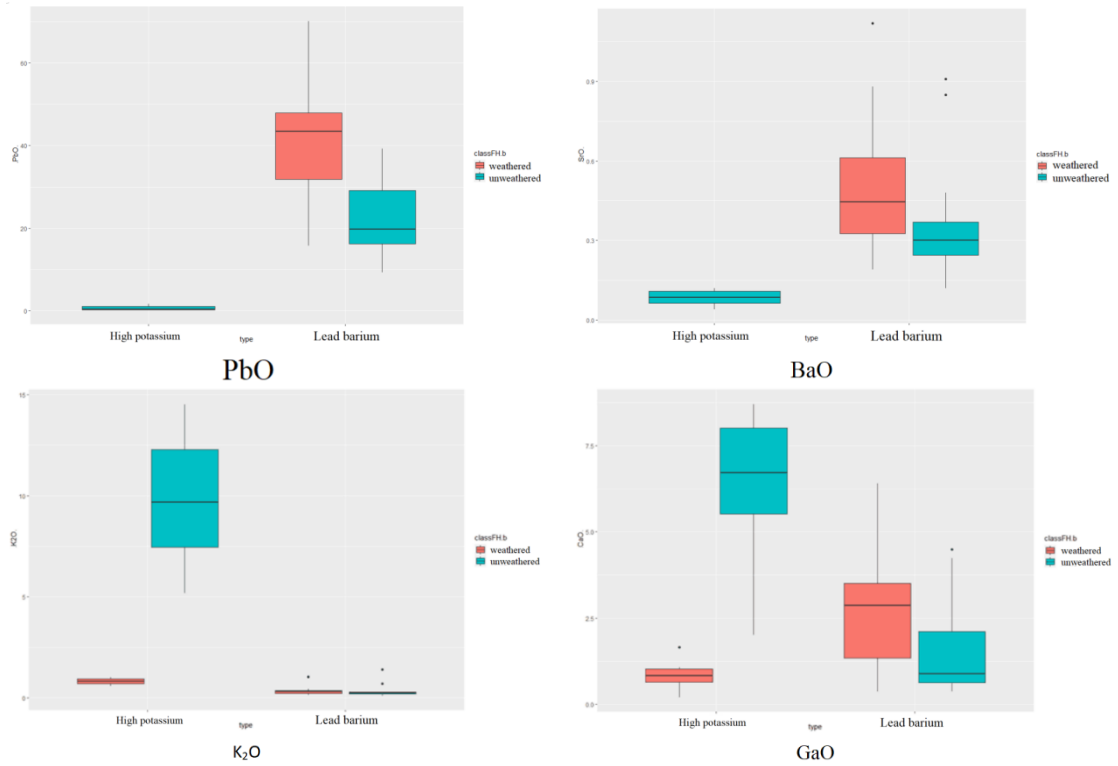

Figure 3. Box-type drawing

For high potassium glass: silica content is extremely high after weathering, over 85%; barium oxide content is extremely low after weathering, almost undetectable; potassium oxide content is high before weathering, but almost gone after weathering; lead oxide content is very low before and after weathering. For lead-barium glass: high silica content before weathering, and reduced after weathering; barium oxide and lead oxide content increased after weathering; potassium oxide content is very low before and after weathering [7].

3.4. The results of subclass division

It is known that we have two types of glass, with 14 chemical components as samples. According to the following view, the chemical components we choose are: calcium oxide, copper oxide, iron oxide and sodium oxide are used for sub-classification.

The following two subclasses of glass are derived:

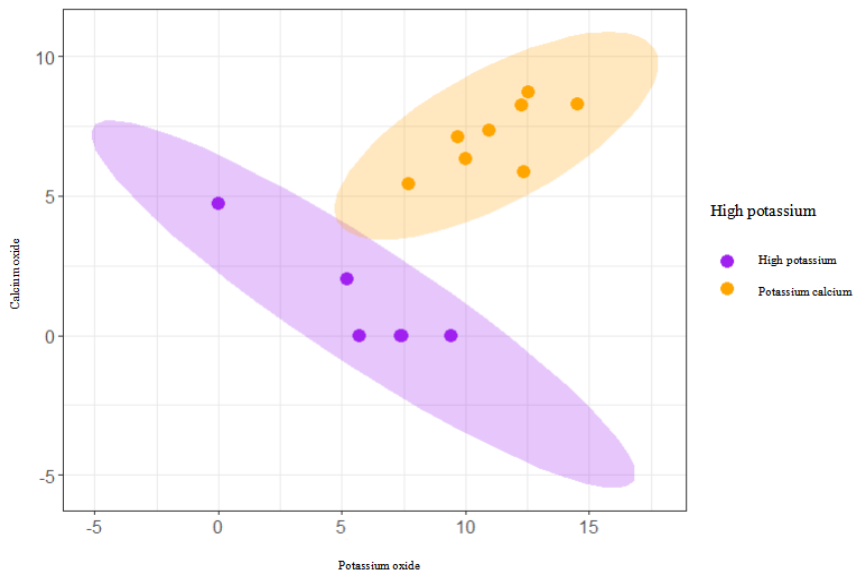

Figure 4. Subdivision of high potassium glass

As can be seen from the Figure 4, some of the high potassium glass species are very high in potassium calcium, which we classify as potassium calcium glass. Lead glass usually contains 18-40% (by weight) lead oxide, while modern lead glass contains at least 24% PbO.

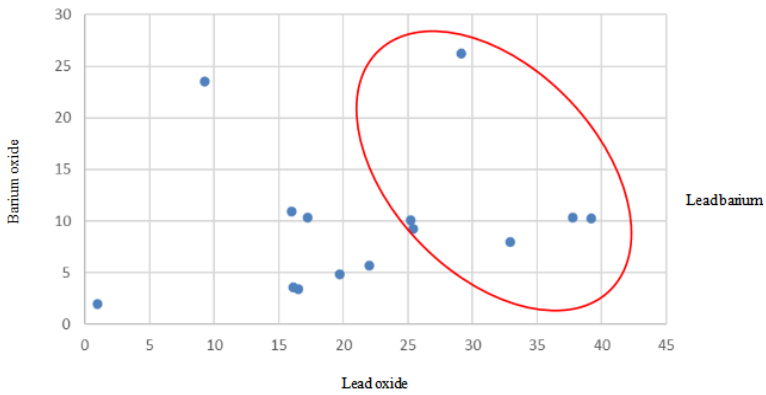

Figure 5. Subdivision of lead barium glass

As can be seen from the Figure 5, some of the lead barium glasses contain very high lead content, which we classify as high lead glass.

By analyzing different chemical elements, we found that the content of calcium oxide is particularly high in potassium glass. By analyzing the scatter plot, the threshold can be set to 5, according to this standard, when calcium oxide. CaO.> 5 as a subclass potassium calcium glass, its calcium content is higher. Potassium calcium glass is an important type in the literature, and high lead glass is an important type in the subsequent development. At the same time, we use the random forest method to cross-verify the classification several times [8].

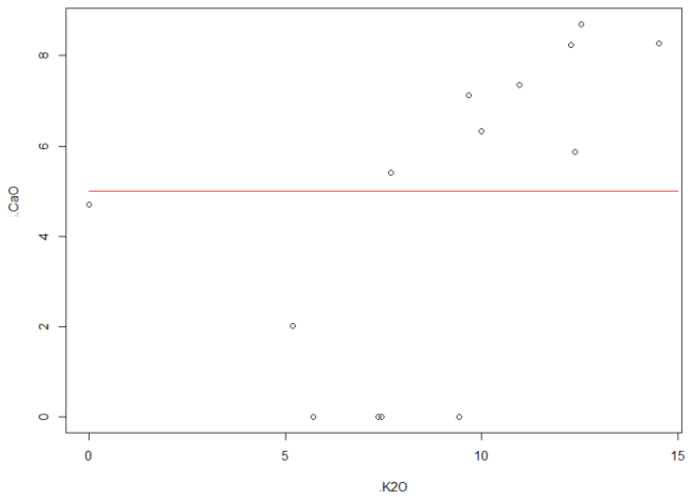

Figure 6. High potassium glass

According to Figure 1, we obtained the sub-class of high potassium glass: calcium potassium glass; Figure 2 shows the subclass of lead barium glass: high lead glass. By comparing the subcategory division we obtained with the professional journals we found on the direction of cultural relics identification, we found that our subcategory division was more accurate and reasonable.

4. Conclusions

The model is applicable to a wide range of fields, analyzing the relationship between the surface weathering of glass artifacts and their glass type, decoration and color, and analyzing the statistical law of the content of chemical components with and without weathering on the surface of artifact samples, which can be applied to the classification of artifacts and the conservation of artifacts;

achieving sub-classification of chemical components of different types of glass before and after weathering, which can be applied to problems such as waste classification, and has a positive effect in saving classification costs and It has a positive effect in saving classification cost and improving economic efficiency.

References

[1] Wen Rui, Cao Shiyuan, LiuRuijun, Zhu Yingpri. Study on the process and composition of glass excavated from the Yemule Site in the Song and Yuan Dynasties of Xinjiang [J]. Journal of Conservation and Archaeological Science, 2019. 31(4): 47-54.

[2] Ren Yubo, Wen Rui, Xian Yiheng, Zhang Cuimin. Study on chemical composition and manufacturing technology of glass earpin unearthed from Han Dynasty Tomb of Yingchengzi [J]. 2022.34(3): 45-54.

[3] Hu Zhizhong, Li Pei, Jiang Manlu, Wang Tongyang, Du Gu, Yang Bo. Composition analysis and production source of ancient glass material LA-ICP-MS [J]. Journal of Rock ore test, 2020.07(01): 505-514.

[4] Roxana Bugoi, Alexandra Ţârlea, Veronika Szilágyi, Ildikó Harsányi, Laurenţiu Cliante, Zsolt Kasztovszky. Chemical analyses on late antique glass finds from Histria, Romania [J]. 31 October 2021.

[5] Li Xulong, Zhang Xia, Lin Chunming, Huang Shuting. A review of common chemical weathering indexes: Application and prospect [J]. Geological journal of universities, 2022.28(01): 51-63

[6] Sun Jigui, Liujie, Zhao Lianyu. Research on clustering algorithm[J], Journal of Software, 2008, 19(1): 48-61.

[7] Dong Junqing. A restudy on the technical origin and development of ancient Chinese glass [D]. University of Chinese Academy of Sciences, 2020.09.

[8] R. Balvanović, Ž. Šmit. Sixth-century AD glassware from Jelica, Serbia—an increasingly complex picture of late antiquity glass composition. Archaeological and Anthropological Sciences. 94 (2020).