A study on the classification of the composition of ancient glassware based on statistical law analysis

Yuexin Pang *

School of semiconductor and physics, North University of China, Taiyuan, China, 030051

* Corresponding Author Email: 2823253247@qq.com

Abstract. Ancient glass is highly susceptible to weathering by the environment in which it is buried, and weathering can cause changes in the proportions of its chemical composition, which can affect the correct determination of its category. In this paper, we solve the problem by studying the chemical composition of ancient glass artefacts to establish a mathematical model. We first used the Spearman correlation test and obtained that the weathering of the surface of the artefacts had no relationship with the color and decoration of the glass, and a negative weak correlation with the type of glass; then we analyzed the statistical pattern of the chemical composition content of the surface of the artefact samples with and without Na_2O CuO BaO SrO SnO_2 SO_2 weathering, and conducted the Mann-Whitney test on the chemical composition of the sample data. The mean values of K_2O, MgO, Fe_2O_3, CuO, BaO, SnO_2 and SO_2 in lead-barium glass were not significantly different before and after weathering, while the mean values of other oxides were significantly different, e.g. the CaO content increased from 1.89% to 4.49% after weathering; finally, the chemical composition of surface weathered glass before weathering was predicted. By analyzing the discrete degree coefficients of each component, we found that the component content is stochastic, and proposed the index of random variation to quantify the stochasticity, and combined with the inevitable variation in the weathering process to establish a mathematical model of the chemical component content before and after weathering for prediction.

Keywords: glass classification, Mann-Whitney test, Spearman correlation test

1. Introduction

Weathering can lead to changes in the proportions of the composition of ancient glass objects, which can affect the correct determination of their category [1]. By studying the chemical composition of ancient glass artefacts. This paper is based on data from a sample of glass artefacts provided by a website. Firstly, we were asked to analyses the relationship between the surface weathering of glass artefacts and their glass type, decoration and color, and we used the Spearman correlation test; then we were asked to analyses the statistical pattern of the chemical composition content of artefact samples with and without weathering: that is, the change in the chemical composition content of high-potassium glass and lead-barium glass before and after weathering, and we conducted normality tests and rank-sum tests on the chemical composition content of the samples to obtain mean values before and after weathering In order to predict the chemical composition content of surface weathered glass before weathering, we proposed the concepts of inevitable variation of weathering process and random variation of weathering process, and also introduced the random variation of process α_{ij} and random variation of weathering β_{ij} to establish the mathematical model of chemical composition content before and after weathering for prediction[2-5]**.**

2. The basic fundamental of Mann Whitney test

In order to further analyses the statistical pattern of the chemical content of the surface of the artefact samples with or without weathering, we divided each type of glass into two groups based on the presence or absence of weathering and checked whether there was a significant difference between the mean values of each chemical content of the two groups, i.e., the data was tested for significance [6].

Unlike the independent sample t-test, the Mann Whitney test does not require the data to be normally distributed, and the frequencies of the categorical chemical components can be unequal [7-8]. The test procedure is as follows.

Formulate the hypothesis thatH_0: The jth chemical composition of glass type i without weathering has the same data with and without weathering:

H_1: the jth chemical composition of glass type i without weathering has different data on the presence or absence of weathering

Two sets of data for the same chemical composition of the same type of glass are mixed and ranked in order of magnitude. The data with the smallest content is ranked as 1, the data with the second smallest content is ranked as 2, and so on (in the case of equal data, the average of these data ranks is taken as the rank).

Find the rank of each of the two groups andW_{0ij}, W_{1ij} . whereW_{0ij} denotes the rank sum of the jth chemical composition data set for glass type i without weathering, andW_{1ij} denotes the rank sum of the jth chemical composition data set for glass type i with weathering.

$$\begin{aligned} W_{0ij} &= \frac{n_{0ij}(N_{ij}+1)}{2} \\ W_{1ij} &= \frac{n_{1ij}(N_{ij}+1)}{2} \end{aligned} \tag{1}$$

n_{0ij} is the sample size of the jth chemical composition data for glass type i without weathering, and n_{1ij} is the sample size of the jth chemical composition data for glass type i with weathering. N_{ij} is the total number of jth chemical composition data samples for glass type i.

Calculation of the Mann-Whitney U-test statistic:

$$W_{ij} = W_{0ij} - n_{0ij}(n_{0ij}+1)/2 \tag{2}$$

$$Z_{ij} = \frac{W_{ij} - n_{0ij} \cdot n_{1ij}/2}{\sqrt{n_{0ij} \cdot n_{1ij}(N_{ij}+1)/12}} \sim N(0,1) \tag{3}$$

ConstructingZ_{ij} statistic with a critical value$Z_{\propto ij}$ (significance level of 0.05) for comparison whenZ_{ij} <$Z_{\propto ij}$ is rejected whenH_0 , accept H_1 .

3. Results

3.1. The establishment of simulation model

A statistical law is a holistic law of random events, not a simple superposition of the characteristics of individual random events, but the inevitability that characterizes a system of events. Laws that work for a large number of contingent events as a whole, expressing the essence and inevitable connection of these things as a whole. We consider the statistical law of the chemical content of the surface of a relic with or without weathering to refer to whether the difference between the mean values of the chemical content of lead-barium glass and high-potassium glass before and after weathering is significant [9-10]. The pattern of change in the content of each chemical component itself before and after weathering. We can see that the chemical composition of the surfaces of the high-potassium and lead-barium glass samples differ, which is related to their type, and that there may also be differences in the content of the composition of random samples from the same artefact surface, which is related to weathering. In order to investigate the statistical pattern of the chemical content of the surface of the artefact samples with and without weathering, we first tested the normality of the data from the Form 2 sampling points.

3.2. Analysis of experimental results

Here we give the mean, standard deviation, maximum and minimum values of the content of each chemical component of high potassium glass and lead-barium glass before and after weathering, some of which are shown in Table 1 below.

Table 1. Changes in chemical composition content of lead barium glass before and after weathering

	Barium lead glass	**(SiO_2)**	**(Na_2O)**	**(K_2O)**	**(CaO)**	**(MgO)**	**(Al_2O_3)**
No weathering	Average value	55.348	1.761	1.098	1.189	0.685	4.253
	Standard deviation	11.788	2.292	2.498	1.301	0.554	3.242
	Minimum value	31.940	0.000	0.000	0.000	0.000	0.000
	Maximum value	79.460	7.920	9.420	4.490	1.670	14.340
	Very poor	47.520	7.920	9.420	4.490	1.670	14.340
Weathered	Average value	29.198	0.201	0.165	2.551	0.639	2.894
	Standard deviation	18.926	0.539	0.284	1.682	0.694	2.553
	Minimum value	3.720	0.000	0.000	0.000	0.000	0.450
	Maximum value	94.290	2.220	1.050	6.400	2.730	13.650
	Very poor	90.570	2.220	1.050	6.400	2.730	13.200

Table 2. Changes in chemical composition of high potash glass before and after weathering

	High Potassium Glass	**(SiO_2)**	**(Na_2O)**	**(K_2O)**	**(CaO)**	**(MgO)**	**(Al_2O_3)**
No weathering	Average value	66.941	0.758	9.323	5.817	1.038	6.945
	Standard deviation	8.364	1.330	4.112	2.724	0.693	2.332
	Minimum value	59.010	0.000	0.000	0.000	0.000	3.930
	Maximum value	87.050	3.380	14.520	8.700	1.980	11.150
	Very poor	28.040	3.380	14.520	8.700	1.980	7.220
Weathered	Average value	93.963	0.000	0.543	0.870	0.197	1.930
	Standard deviation	1.734	0.000	0.445	0.488	0.306	0.964
	Minimum value	92.350	0.000	0.000	0.210	0.000	0.810
	Maximum value	96.770	0.000	1.010	1.660	0.640	3.500
	Very poor	4.420	0.000	1.010	1.450	0.640	2.690

Analyzing the two tables above and combining the results of the rank sum test, we can obtain the following statistical pattern of chemical composition before and after weathering. For high potassium glasses: weathering has a direct and inevitable effect on the content of SiO_2 , K_2O , CaO , MgO , Al_2O_3 , Fe_2O_3 , PbO .The compositional content of P_2O_5 、 SiO_2 varies from 66.94% to 93.96%, K_2O from 0.54% to 9.323%, CaO from 0.87% to 5.817%, MgO from 0.197% to 1.038%, Al_2O_3 from 1.93% to 6.945%, from 0.265% to 2.107%, from 0% to 0.449%, from 0% to 6.945%, from 0.265% to 0.449%, from 0% to 0.945%, from 0.265% to 0.449%. 6.945%, 0.265%-2.107% for Fe_2O_3 , 0%-0.449% for PbO , and 0.28%-1.406% for P_2O_5 . This indicates that the majority of K_2O was precipitated out of the surface glass during the weathering process and the content of SiO_2 increased significantly.

For barium lead glass: weathering has a direct and inevitable effect on the content of SiO_2 , Na_2O , CaO , Al_2O_3 , PbO , P_2O_5 . The compositional content of SrO SiO_2 varies from 29.2% to 55.35%, Na_2O varies from 0.21% to 1.761%, CaO varies from 1.819% to 2.551%, Al_2O_3 varies from 2.89% to 4.25%, PbO varies from 19.69% to 40.79%, varies from 1.032% to 4.910% and varies from 0.25% to 0.389%. 40.79%, 1.032% to 4.910% for P_2O_5 and 0.25% to 0.389% for SrO . This indicates that Si and Ca are lost from the inside to the outside of the weathering layer, and the content of Pb decreases from the outside to the inside.

Testing the normality of chemical component data in sample data is generally done using the graphical method, which visually demonstrates normality, but the amount of data in the sample is less than 100, so we use skewness and kurtosis to determine the normality distribution of the sample. When using the skewness and kurtosis of a variable for normality testing, the A-score (skewness A-score and kurtosis A-score) can be calculated for skewness and kurtosis respectively[11].

Some of the chemical composition data are 0, resulting in no A-score being calculated, so 0 is used instead in the table. At a test level of $\alpha = 0.05$, see if the skewness and kurtosis A-score satisfy the condition restricted to between ±1.96. If one of the skewness and kurtosis A-scores is not satisfied then the distribution is not considered to be normal. It can be seen that the skewness and kurtosis A-score are not both between ±1.96 and therefore the chemical composition of the data in the Annexes does not satisfy a normal distribution.

The above normality test showed that the chemical composition content of each type of glass surface with or without weathering was not normal overall. In order to further analyses the statistical pattern of the chemical composition content of the surface of the artefact samples with or without weathering, we divided each type of glass into two groups based on the presence or absence of weathering and checked whether there was a significant difference between the mean values of each chemical composition content of the two groups, i.e., a significance test was performed on the data.

Unlike the independent sample t-test, the Mann Whitney test does not require the data to be normally distributed and the frequencies of the categorical chemical components can be unequal.

The results of the partial tests for each type of glass are shown in Table 3 below.

Table 3. Mann Whitney test statistics

High potassium glass Mann Whitney test statistics									
	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3	CuO	PbO
Z-statistic	-3.317	-1.360	-2.821	-2.714	-2.363	-3.317	-2.714	-1.508	-2.363
Asymptotic saliency (two-tailed)	0.001	0.174	0.005	0.007	0.018	0.001	0.007	0.131	0.018
Barium lead glass Mann Whitney test statistics									
	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3	CuO	PbO
Z-statistic	-5.007	-3.027	-1.799	-3.166	-0.504	-2.156	-0.084	-1.836	-4.677
Asymptotic saliency (two-tailed)	0.000	0.002	0.072	0.002	0.614	0.031	0.933	0.066	0.000

Analysis of the above table shows that

(1) At the 0.05 test level, the mean values of Na_2O, CuO, BaO, SrO, SnO_2 and SO_2 in high potassium glass did not differ before and after weathering, suggesting that weathering does not necessarily have a differential effect on the content of these chemical components, due to the minimal content of CuO, BaO, SrO, SnO_2 and SO_2 in high potassium glass and the fact that Na_2O, SnO_2 and SrO are chemically stable and less susceptible to weathering.

(2) At a test level of 0.05, the mean values of K_2O, MgO, Fe_2O_3, CuO, BaO, SnO_2 and SO_2 in lead-barium glass do not differ before and after weathering, indicating that weathering does not necessarily have a differential effect on the content of these chemical components, due to the low content of K_2O, MgO, Fe_2O_3, CuO and SO_2 in lead-barium glass and the fact that BaO and SnO_2 are chemically stable and less susceptible to weathering.

4. Conclusions

This paper describes the process of classifying ancient glass with a degree of accuracy and ingenuity, firstly using the Spearman correlation test to analyses the relationship between the surface weathering of glass artefacts and their glass type, decoration and color; then requiring analysis of the statistical pattern of the chemical composition content of artefact samples with and without weathering on the surface to discover chemical compositions with no significant difference in mean values before and after weathering; in order to predict the chemical composition content of surface weathered glass before weathering, a mathematical model of the chemical composition content before and after weathering was developed for prediction. In order to predict the chemical composition content of surface weathered glass before weathering, a mathematical model of the chemical composition content before and after weathering was developed for prediction. In order to predict the chemical composition of surface weathered glass before weathering, a mathematical model was developed to predict the chemical composition before and after weathering.

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