

Composition Analysis and Identification of Ancient Glass Products based on Correlation Analysis and Linear Regression

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Abstract

Ancient glass is very easy to weathering in the process of long-time burial, resulting in the change of its composition, and then affect the identification of glass cultural relics. Therefore, in this paper, Spearman correlation analysis is used to solve the composition analysis of ancient glass products. Descriptive statistical methods and Spearman correlation analysis were used to study the statistical rule of the chemical composition content of cultural relics samples. In addition, mathematical models were established to predict the chemical composition content before and after weathering using the average value and content sum.

Keywords

Glass Relics; Model; Weathering; Composition.

1. Introduction

The main raw material of glass is quartz sand, but the chemical composition of glass with similar appearance is not necessarily the same, and the chemical composition content of different types of glass is significantly different [1]. Ancient glass is easily weathered due to long time of burial or the influence of the buried environment [2]. In the process of weathering, the chemical composition of the glass interior is exchanged with the chemical composition of the buried environment, which leads to the change of the composition proportion, thus affecting the correct judgment of its category[3][4].

Based on a batch of relevant data of ancient Chinese glass relics, archeologists have classified them into two types: high-potassium glass and lead-barium glass according to the proportion of chemical composition and other detection methods. The main purpose of this paper is a preliminary analysis the presence of weathering on the surface of a cultural relics of the samples were analyzed and predicted its chemical composition content of weathering before chemical component content.

2. Model Establishment

2.1. Basic Principle of Spearman Correlation Analysis

X and Y are defined as two groups of data with the same distribution and independence. The number of data elements in the two groups is N. In the two groups of random variables, the i th ($1 \leq i \leq N$) value is represented by X_i and Y_i respectively. Sort X and Y in descending or ascending order at the same time to get two element ranking sets x and y . The elements x_i and y_i are the ranking of X_i in X and Y_i in Y. The difference of the corresponding elements in the set x and y constitutes the ranking difference set d , where $d_i = x_i - y_i$, ($1 \leq i \leq N$). The Spearman correlation coefficient between Y can be calculated by x y or d . The r_s is calculated as Eq. (1) follows [5]:

$$r_s = \frac{\sum_{i=1}^N (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^N (x_i - \bar{x})^2 \sum_{i=1}^N (y_i - \bar{y})^2}} \tag{1}$$

The value range of Spearman correlation coefficient is [- 1, 1]. The greater the absolute value of rs, the stronger the correlation. When Spearman correlation coefficient rs<0, it is considered that there is a negative correlation between the two groups of variables discussed.

2.2. Chemical Composition Content Prediction

In this paper, based on descriptive statistics and using Spearman algorithm to calculate the correlation between each chemical component and whether the cultural relics are weathered, we analyze the change rule of whether there is weathering chemical component content on the surface of cultural relics, and solve the statistical rule to obtain the formula for predicting the content of each component before the weathering of cultural relics (Eq. (2)):

$$\begin{cases} x_{forecast\ medium\ term\ value\ i} = \frac{\bar{x}_{without\ weathering}}{\bar{x}_{weathering}} \cdot x_{before\ the\ predicted\ i} (\bar{x}_{after\ weathering\ i} \neq 0) \\ x_{forecast\ medium\ term\ value\ i} = \bar{x}_{without\ weathering\ i} (x_{after\ weathering\ i} = 0) \end{cases} \tag{2}$$

Wherein, $\bar{x}_{without\ weathering}$ is the average content of a certain component before weathering of this type of cultural relics, and $\bar{x}_{weathering}$ is the average content of a certain component after weathering of this type of cultural relics.

In order to ensure that the sum of the predicted proportions of each component is within the effective area and that the calculation dimensions of the same cultural relic sample before and after weathering are the same, the prediction formula should have the following constraints (Eq. (3)):

$$\sum_{i=1}^n x_{final\ predicted\ value\ i} \tag{3}$$

That is, use the above formula to standardize the predicted value of each component, and the final solution formula is as Eq. (4) shows:

$$x_{final\ predicted\ value\ i} = \frac{\bar{x}_{without\ weathering}}{\bar{x}_{weathering}} \cdot x_{before\ the\ predicted\ i} \cdot \frac{\sum_{i=1}^n x_{before\ the\ predicted\ i}}{\sum_{i=1}^n x_{forecast\ medium\ term\ value\ i}} \tag{4}$$

3. Results and Analysis

3.1. Effect of Weathering on Composition of Different Types of Glass

The correlation analysis of chemical composition of high potassium and lead barium glasses is shown in Table 1 and Table 2.

Table 1. Correlation analysis between chemical composition and weathering of high potassium glass

Chemical component	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃
Correlation coefficient	0.818***	-0.315	-0.706***	-0.545**	-0.602***	-0.795***	-0.545**
Chemical component	CuO	PbO	BaO	P ₂ O ₅	SrO	SnO ₂	SO ₂
Correlation coefficient	-0.273	-0.543**	-0.374	-0.602***	-0.487**	-0.171	-0.315

Note: *** is P≤0.01, ** is P ≤0.05, * is P≤0.1

Table 2. Correlation analysis between chemical composition and weathering of lead barium glass

Chemical component	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃
Correlation coefficient	-0.857***	-0.380**	-0.241	-0.387***	-0.066	-0.394***	-0.068
Chemical component	CuO	PbO	BaO	P ₂ O ₅	SrO	SnO ₂	SO ₂
Correlation coefficient	0.370**	0.734***	0.160	0.564***	0.413***	-1.460	0.320**

Note: *** is P≤0.01, ** is P ≤0.05.

For high potassium type glass, weathering is significantly related to the content of silica SiO₂, potassium oxide K₂O, calcium oxide CaO, magnesium oxide MgO, alumina Al₂O₃, iron oxide Fe₂O₃, lead oxide PbO, phosphorus pentoxide P₂O₅, strontium oxide SrO.

For lead barium glass, weathering is significantly related to the content of silica SiO₂, sodium oxide Na₂O, calcium oxide CaO, alumina Al₂O₃, copper oxide CuO, lead oxide PbO, phosphorus pentoxide P₂O₅, strontium oxide SrO, sulfur dioxide SO₂.

3.2. Prediction of Chemical Composition Content of Cultural Relics before Weathering

The statistical analysis results of chemical composition content of high-potassium glass and lead-barium glass before and after weathering are shown in Table 3 and 4. The prediction results of chemical composition of high potassium glass and lead barium glass are shown in Table 5 and Table 6.

Table 3. Change law of descriptive statistical analysis of chemical composition of high potassium glass before and after weathering

Chemical component	Weathering conditions	sample size	mean	standard deviation	variance	kurtosis	skewness
SiO ₂	B	12	67.984	8.755	76.652	0.536	1.158
	A	6	93.963	1.734	3.005	-0.388	0.854
Na ₂ O	B	12	0.695	1.28692	1.656	0.559	1.497
	A	6	0	0	0	0	0
K ₂ O	B	12	9.3308	3.9203	15.369	1.9	-1.203
	A	6	0.5433	0.44518	0.198	-1.913	-0.537
CaO	B	12	5.3325	3.09248	9.563	-0.518	-0.875
	A	6	0.87	0.48777	0.238	0.988	0.504
MgO	B	12	1.0792	0.67614	0.457	-1.015	-0.434
	A	6	0.1967	0.30631	0.094	-1.598	1.014
Al ₂ O ₃	B	12	6.62	2.49151	6.208	-0.492	0.482
	A	6	1.93	0.96449	0.93	0.181	0.779
Fe ₂ O ₃	B	12	1.9317	1.66669	2.778	2.568	1.176
	A	6	0.265	0.0695	0.005	-1.418	-0.3
CuO	B	12	2.4525	1.65999	2.756	-1.058	0.101
	A	6	1.5617	0.93482	0.874	2.231	1.218

PbO	B	12	0.4117	0.58899	0.347	0.418	1.374
	A	6	0	0	0	0	0
BaO	B	12	0.5983	0.9821	0.965	1.238	1.493
	A	6	0	0	0	0	0
P ₂ O ₅	B	12	1.4025	1.43396	2.056	1.876	1.678
	A	6	0.28	0.20995	0.044	0.372	0.399
SrO	B	12	0.0417	0.0484	0.002	-1.452	0.571
	A	6	0	0	0	0	0
SnO ₂	B	12	0.1967	0.68127	0.464	12	3.464
	A	6	0	0	0	0	0
SO ₂	B	12	0.1017	0.18551	0.034	0.055	1.396
	A	6	0	0	0	0	0

Note: B means “Before weathering”, A means “After weathering”.

Table 4. Descriptive statistical analysis of chemical composition of lead-barium glass before and after weathering

Chemical component	Weathering conditions	sample size	mean	standard deviation	variance	kurtosis	skewness
SiO ₂	B	23	54.6596	11.82859	139.916	-0.538	-0.371
	A	26	24.9127	10.60548	112.476	1.23	0.313
Na ₂ O	B	23	1.6826	2.37164	5.625	0.758	1.287
	A	26	0.2162	0.55665	0.31	6.743	2.666
K ₂ O	B	23	0.2187	0.31006	0.096	10.061	2.883
	A	26	0.1335	0.23997	0.058	7.793	2.512
CaO	B	23	1.3204	1.2847	1.65	1.03	1.347
	A	26	2.6954	1.65978	2.755	-0.461	0.383
MgO	B	23	0.6404	0.54675	0.299	-1.241	0.085
	A	26	0.65	0.70643	0.499	1.209	1.037
Al ₂ O ₃	B	23	4.4561	3.26245	10.644	4.233	1.988
	A	26	2.97	2.63427	6.939	10.638	2.829
Fe ₂ O ₃	B	23	0.7365	1.15473	1.333	4.768	2.072
	A	26	0.5846	0.73653	0.542	1.525	1.404
CuO	B	23	1.4317	1.96987	3.88	6.877	2.461
	A	26	2.2758	2.82052	7.955	4.154	2.101
PbO	B	23	22.0848	8.21515	67.489	-0.456	0.62
	A	26	43.3138	12.23022	149.578	0.233	-0.033
BaO	B	23	9.0017	5.82528	33.934	3.758	1.797
	A	26	11.8073	9.97827	99.566	0.838	1.278

P ₂ O ₅	B	23	1.0491	1.84706	3.412	3.724	2.167
	A	26	5.2773	4.1967	17.612	-0.824	0.4
SrO	B	23	0.2683	0.24345	0.059	1.96	1.231
	A	26	0.4185	0.26484	0.07	0.777	0.544
SnO ₂	B	23	0.0465	0.12734	0.016	5.816	2.634
	A	26	0.0685	0.26945	0.073	19.787	4.365
SO ₂	B	23	0.1591	0.76316	0.582	23	4.796
	A	26	1.3662	4.20607	17.691	9.634	3.261

Note: B means “Before weathering”, A means “After weathering”.

Table 5. Prediction of chemical composition of high potassium glass

Heritage sampling points	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃
07	72.789	0.755	0.000	7.123	0.000	7.376	1.346
09	71.617	0.724	10.555	3.959	0.000	4.717	2.430
10	73.452	0.729	16.575	1.350	0.000	2.915	1.988
12	66.278	0.675	16.851	4.287	0.000	4.865	2.054
22	59.803	0.622	11.374	9.107	3.143	10.745	2.283
27	71.938	0.745	0.000	6.178	3.178	9.232	1.563
Heritage sampling points	CuO	PbO	BaO	P ₂ O ₅	SrO	SnO ₂	SO ₂
07	5.526	0.447	0.650	3.318	0.045	0.214	0.110
09	2.536	0.429	0.623	1.826	0.043	0.205	0.106
10	1.384	0.432	0.628	0.000	0.044	0.206	0.107
12	2.517	0.400	0.581	0.730	0.040	0.191	0.099
22	0.773	0.368	0.536	0.941	0.037	0.176	0.091
27	2.593	0.441	0.642	1.934	0.045	0.211	0.109

Table 6. Prediction of chemical composition of lead barium glass

Heritage sampling points	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃
02	66.796	0.000	1.425	0.914	0.943	7.946	2.026
08	49.719	0.000	0.000	0.775	0.000	2.492	0.000
08 Severe weathering point	18.288	0.000	0.000	2.684	0.000	3.317	0.000
11	65.410	0.000	0.301	1.449	0.600	3.945	0.000
26	49.278	0.000	0.000	0.760	0.000	1.313	0.000
26 Severe weathering point	14.772	0.000	1.171	2.535	0.000	3.529	0.000
34	68.000	0.000	0.350	0.314	0.000	2.319	0.528
36	63.220	11.726	0.165	0.125	0.000	1.925	0.302

38	60.301	8.355	0.000	0.264	0.000	3.545	0.314
39	60.468	0.000	0.000	0.542	0.000	0.868	0.000
41	45.521	0.000	0.800	2.594	2.921	6.185	2.611
43 point 1	35.725	0.000	0.000	3.199	1.116	4.879	1.294
43 point 2	53.471	0.000	0.000	3.344	1.016	6.329	2.026
49	58.948	0.000	0.000	1.989	1.306	8.297	3.319
50	45.796	0.000	0.000	1.723	0.519	3.587	0.497
51 point 1	53.760	0.000	0.000	1.658	1.128	8.638	1.538
51 point 2	52.412	0.000	0.000	2.670	1.544	4.641	0.610
52	53.491	8.382	0.000	1.000	0.496	1.816	0.283
54	52.954	0.000	0.561	1.608	1.320	7.429	0.000
54 Severe weathering point	47.444	0.000	0.000	0.000	1.335	7.623	0.000
56	59.844	0.000	0.000	0.527	0.000	2.861	0.000
57	54.981	0.000	0.000	0.601	0.000	3.551	0.000
Heritage sampling points	CuO	PbO	BaO	P ₂ O ₅	SrO	SnO ₂	SO ₂
02	0.126	19.064	0.000	0.560	0.093	0.000	0.000
08	6.634	15.457	23.475	0.756	0.244	0.000	0.270
08 Severe weathering point	3.215	28.106	36.986	2.557	0.561	0.000	2.530
11	2.478	10.794	8.663	1.558	0.192	0.000	0.000
26	6.794	16.053	24.452	0.665	0.299	0.000	0.207
26 Severe weathering point	3.690	25.938	42.865	2.045	0.657	0.000	2.687
34	0.740	19.314	5.787	0.055	0.116	0.000	0.000
36	0.280	14.513	5.269	0.100	0.094	0.000	0.000
38	0.345	19.712	5.459	0.0750	0.200	0.000	0.000
39	0.523	30.691	5.064	0.229	0.375	0.000	0.000
41	0.121	0.121	7.328	1.569	0.309	0.000	0.000
43 point 1	3.976	37.614	6.390	0.000	0.492	0.000	0.000
43 point 2	0.960	24.073	2.446	2.696	0.309	0.000	0.000
49	0.370	15.278	3.803	1.938	0.251	0.000	0.000
50	0.743	24.466	11.013	1.377	0.449	0.000	0.000
51 point 1	0.773	19.190	5.947	1.509	0.227	0.962	0.000
51 point 2	0.475	27.515	0.000	1.832	0.000	0.000	0.000
52	0.375	21.513	5.467	1.012	0.244	0.000	0.000
54	0.509	28.777	5.095	0.859	0.558	0.000	0.000
54 Severe weathering point	0.959	35.389	0.000	3.341	0.829	0.000	0.000
56	0.419	18.488	9.658	0.445	0.000	0.000	0.000
57	0.648	21.295	11.394	0.000	0.000	0.000	0.000

4. Conclusion

With a long time of burial, ancient glass is very easy to be weathered in this process, and its composition is extremely easy to change, which will affect the identification of glass cultural relics. Therefore, this paper tries to solve the problem of composition analysis of ancient glass products by using mathematical model. The correlation analysis of chemical composition of high potassium and lead barium glasses was analyzed. In addition, the composition of glass relics before weathering is predicted. This paper provides some research basis for the analysis of the composition of glass before weathering.

References

- [1] WANG Chengyu; TAO Ying. THE WEATHERING OF SILICATE GLASSES [J]. Journal of The Chinese Ceramic Society,2003(1): 78-85.
- [2] Fuxi Gan. SOME CONSIDERATIONS ABOUT RESEARCH OF CHINESE ANCIENT GLASSES[J]. Journal of the Chinese Ceramic Society,2004(02):182-188.
- [3] LI Qinghui; GAN Fuxi; GU Donghong. Some Questions Related to the Research of Ancient Chinese Glasses [J]. Studies in the History of Natural Sciences,2007(02):234-247.
- [4] ZHANG Liyan; LI Hong; CHEN Shubin; LI Zhongdi; RUAN Minzhi; XUE Tianfeng; QIAN Min; FAN Sijun. Simulation Methods of Glass Composition and Properties: A Short Review [J]. Journal of the Chinese Ceramic Society,2022,50(08):2338-2350.
- [5] WANG Xiaoyan; LI Meizhou. The Relationship of Rank Correlation Coefficient and Spearman Rank Correlation Coefficient [J]. Journal of Guangdong Industry Technical College,2006(04):26-27.