Composition analysis and identification of ancient glass products

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Abstract. Ancient glass 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 their composition ratios, which affect the correct judgment of their categories. In this paper, the identification of properties and category analysis of ancient glass are realized by processing known data with chi-square test, multiple linear regression analysis, R-type cluster analysis, and correlation coefficient method.

Keywords: Glass component test, chi-square test, multiple linear regression analysis, spearman correlation coefficient, R-type cluster analysis.

1. Introduction

Glass has a long history, it is one of the first man-made materials invented by man and one of the most expensive materials. Glass was born in the two river valleys of Western Asia, ancient Egypt, ancient Rome will be carried forward. Chinese glass appeared later, dating back to the Western Zhou period. The Chinese revered jade, and ceramics as a practical container, so glass has not been the main artifacts of society as well as practical ware. However, glass production has been developed throughout Chinese history, and can be said to be a witness to the change of Chinese craft technology and aesthetic culture [1].

Glass and the role of the atmosphere erosion is called weathering, glass weathering resistance refers to the ability to resist weathering, glass buried in the soil (such as burial objects in ancient tombs) by erosion, also known as weathering. After the weathering of glass, the surface of the weathering film, due to the refractive index of the film layer and the glass matrix is different, iridescence formed by light exposure. Most cases are weathering products accumulate on the surface of the glass to form white spots or large patches of mist [2]. Ancient glass 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 the proportion of its composition, which affects the correct judgment of its category. Therefore, this paper selects mathematical models for modeling to model glass types and identify problems related to chemosynthetic composition.

2. Modeling and solving of glass weathering and types, ornamentation and color

2.1. Chi-square test and results

According to the basic information of cultural relics, the type, decoration and color of glass cultural relics are categorical variables. To compare the sample rates of more than two samples and the correlation analysis of categorical variables, chi-square test is used to test the correlation between multiple discrete random variables [3], that is, the correlation is obtained by testing and denying the independence between them, as shown in Table 1.

Table 1. Chi-square test table.

		whether the weathering		total	x^2	p
		unweathered	weathered			
sculpture type	A	11	11	22	4. 9565	0. 0839
	B	0	6	6		
	C	13	17	30		
total		24	34	58		
element type	high K	12	6	18	6. 8804	0. 0087
	lead-barium	12	28	40		
total		24	34	58		
color	black	0	4	4	8. 2332	0. 3125
	blue and green	6	9	15		
	Cambridge	8	14	22		
	light green	2	1	3		
	dark green	3	4	7		
	purple	2	2	4		
	green	1	0	1		
	dark blue	2	0	2		
total		24	34	58		

The p value is calculated by chi-square test, and the null hypothesis H0 can be accepted within the confidence interval of 0.05: this property index is correlated with weathering or not; if $p>0.5$, the null hypothesis will be rejected; the smaller the value of p, the more relevant it is. Therefore, the correlation with weathering or not is from the largest to the smallest for glass type, decoration and color.

2.2. Frequency histogram and statistical law

The average, standard deviation, median, variance, kurtosis and skewness of each chemical composition were calculated according to the chemical composition proportion form. The frequency distribution histograms of relatively important chemical components before and after weathering of lead-barium glass and high-potassium glass were drawn for comparative analysis, as shown in Table 2 and Figure 1.

Table 2. Chemical composition statistics of lead-barium glass before and after weathering.

Element	Whether the weathering	Quantity	Mean	std	IQR	var	KURT	Skewness
SiO2	weathered	24	26.642	8.848	25.58	78.285	1.896	1.001
	unweathered	23	54.660	11.569	54.61	133.832	-0.538	-0.346
Na2O	weathered	24	0.234	0.564	0	0.319	5.959	2.368
	unweathered	23	1.683	2.320	0	5.380	0.758	2.520
K2O	weathered	24	0.128	0.237	0.15	0.056	8.7211	2.520
	unweathered	23	0.219	0.303	0	0.092	0.061	2.691
CaO	weathered	24	2.662	1.689	2.58	2.854	-0.609	0.408
	unweathered	23	1.320	1.256	0.84	1.579	1.030	1.257
MgO	weathered	24	0.704	0.694	0.65	0.481	1.135	0.885
	unweathered	23	0.640	0.535	0.71	0.286	-1.241	0.080
Al2O3	weathered	24	3.122	2.632	2.54	6.928	10.129	2.582
	unweathered	23	4.456	3.191	3.86	10.181	4.233	1.856
Fe2O3	weathered	24	0.633	0.731	0.325	0.534	1.257	1.223
	unweathered	23	0.737	1.294	0	1.275	4.768	1.934
CuO	weathered	24	2.185	2.859	1.005	8.174	4.167	2.029
	unweathered	23	1.432	1.927	0.65	3.712	6.877	2.298
PbO	weathered	24	44.325	11.933	44.435	142.397	0.559	-0.198
	unweathered	23	22.085	8.035	20.12	64.554	-0.456	0.579
BaO	weathered	24	10. 04	7. 909	8. 15	62. 548	2. 969	1. 476
	unweathered	23	9. 002	5. 697	8. 99	32. 459	3. 758	1. 678
P2O5	weathered	24	5. 150	4. 253	3. 915	18. 089	0. 8933. 725	0. 452
	unweathered	23	1. 049	1. 806	0. 19	3. 263		2. 023
SrO	weathered	24	0. 405	0. 266	0. 4	0. 071	0. 8751. 960	0. 644
	unweathered	23	0. 268	0. 238	0	0. 057		1. 149
SnO2	weathered	24	0. 074	0. 274	0	0. 075	18. 18	3. 920
	unweathered	23	0. 047	0. 125	0	0. 016	5. 816	2. 459
SO2	weathered	24	0. 189	0. 634	0	0. 402	10. 23	3. 122
	unweathered	23	0. 159	0. 746	0	0. 557	23	4. 477

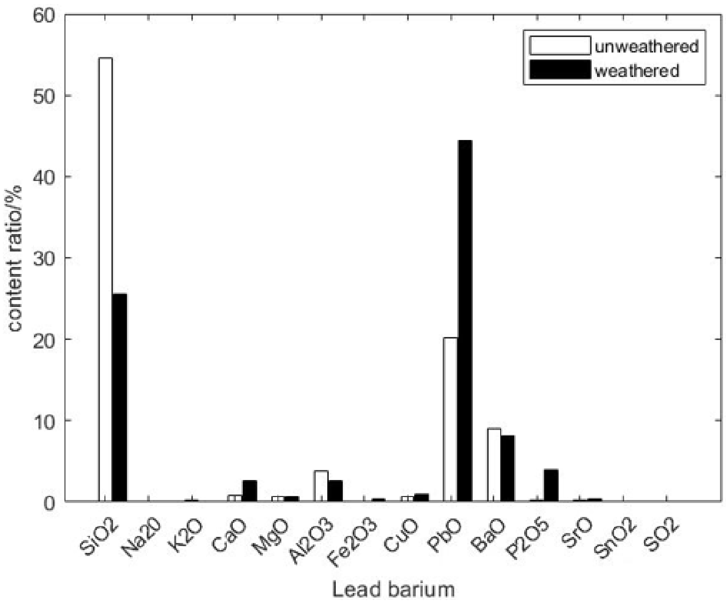

Figure 1. Comparison of chemical composition of Pb and barium glass without weathering.

Table 3. Chemical composition statistics of high potassium glass before and after weathering.

	Whether the weathering	Quantity	Mean	std	IQR	var	KURT	Skewness
SiO_2	weathered	12	68.555	8.529	65.88	3.005	0.231	0.879
	unweathered	6	93.963	1.583	93.505	2.505	-0.388	0.624
Na_2O	weathered	12	0.758	1.268	0	1.608	0.089	1.169
	unweathered	6	0	0	0	0	0	0
K_2O	weathered	12	0.543	0.445	0.665	0.198	-1.913	-0.537
	unweathered	6	0.543	0.406	0.665	10.165	-1.913	0.392
CaO	weathered	12	0.87	0.488	0.83	0.238	0.988	0.504
	unweathered	6	5.333	3.092	6.095	9.563	-0.518	-0.875
MgO	weathered	12	0.197	0.306	0	0.094	-1.598	1.014
	unweathered	6	1.079	0.676	1.165	0.457	-1.015	-0.434
Al_2O_3	weathered	12	1.93	0.964	1.72	0.93	0.181	0.779
	unweathered	6	6.62	2.492	6.185	6.208	-0.492	0.482
Fe_2O_3	weathered	12	0.265	0.069	0.275	0.005	-1.418	-0.3
	unweathered	6	1.932	1.667	2.11	2.778	2.568	1.176
CuO	weathered	12	1.562	0.935	1.545	0.874	2.231	1.218
	unweathered	6	2.452	1.66	2.345	2.756	-1.058	0.101
PbO	weathered	12	0	0	0	0	0	0
	unweathered	6	0.412	0.589	0.155	0.347	0.418	1.374
BaO	weathered	12	0	0	0	0	0	0
	unweathered	6	0.598	0.982	0	0.965	1.238	1.493
P_2O_5	weathered	12	0.28	0.21	0.28	0.044	0.372	0.399
	unweathered	6	1.402	1.434	1.02	2.056	1.876	1.678
SrO	weathered	12	0	0	0	0	0	0
	unweathered	6	0.042	0.048	0.02	0.002	-1.452	0.571
SnO_2	weathered	12	0	0	0	0	0	0
	unweathered	6	0.197	0.681	0	0.464	12	3.464
SO_2	weathered	12	0	0	0	0	0	0
	unweathered	6	0.102	0.186	0	0.034	0.055	1.396

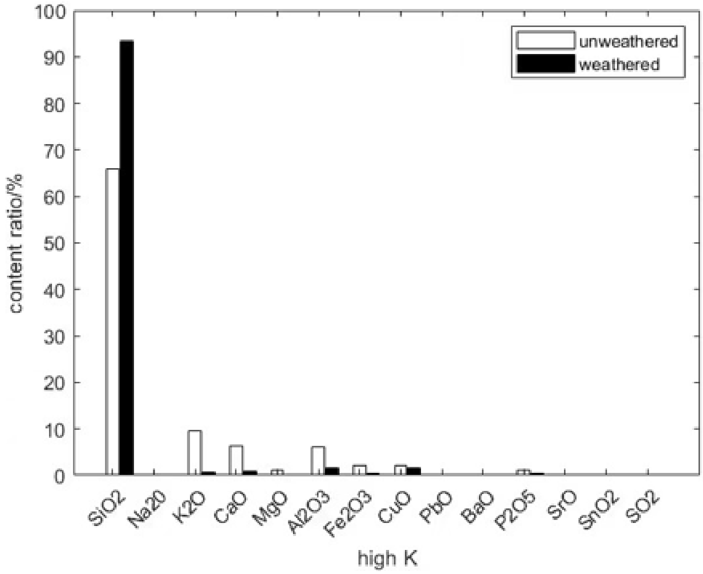

Figure 2. Comparison of chemical composition of high potassium glass without weathering.

The results show that the content of silica decreases significantly and the content of lead oxide increases significantly after weathering. The content of silica and the content of potassium oxide, calcium oxide and alumina in high potassium glass decreased significantly, as shown in Table 3 and Figure 2.

2.3. Multiple linear regression analysis and prediction results

By different elements and silica content make the unweathered scatterplot found linearly related, and some chemical composition not little change after weathering, so by linear regression analysis to forecast the unweathered chemical composition, cultural relics can be divided into high potassium unweathered, high potassium after weathering, lead barium unweathered and lead barium four groups for analysis after weathering, unweathered as raw data, The weathering data are the data to be predicted. The fitting curve is drawn and the goodness of fit is calculated, as shown in Figure 3, Figure 4, Figure 5, Figure 6 and Figure 7. The contents of other unweathered chemical components are predicted by the weathering data, and the spearman correlation coefficient is calculated to verify the results [4] [5], as shown in Table 4 and Table 5.

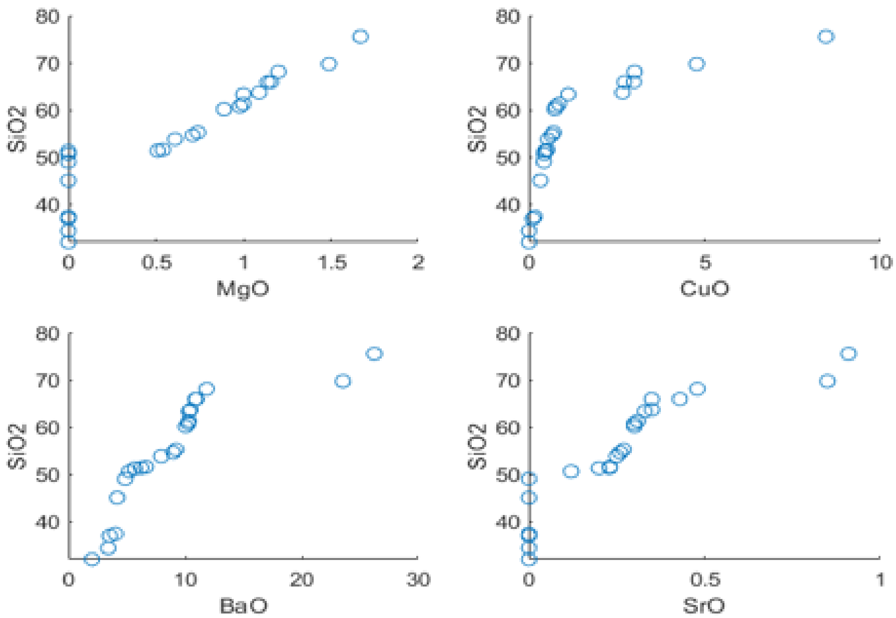

Figure 3. Scatter plot of magnesium oxide, copper oxide, barium oxide, strontium oxide andsilicon oxide in lead barium.

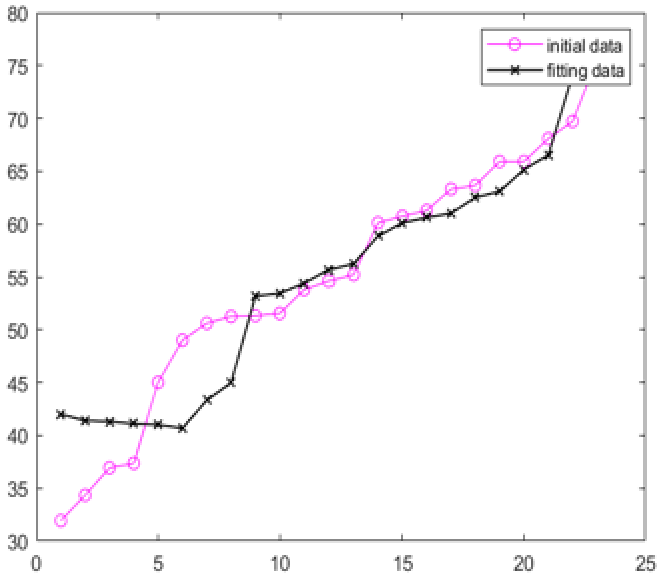

Figure 4. Fitting curves of magnesium oxide and silica (left).

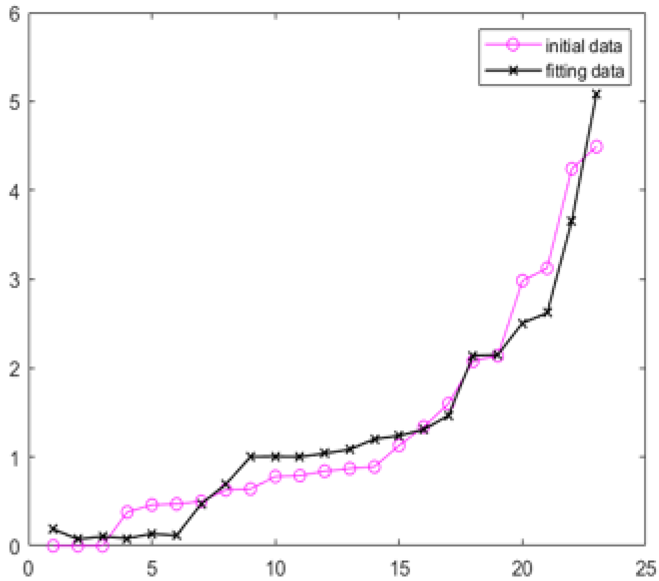

Figure 5. Fitting curve of copper oxide and silica (right).

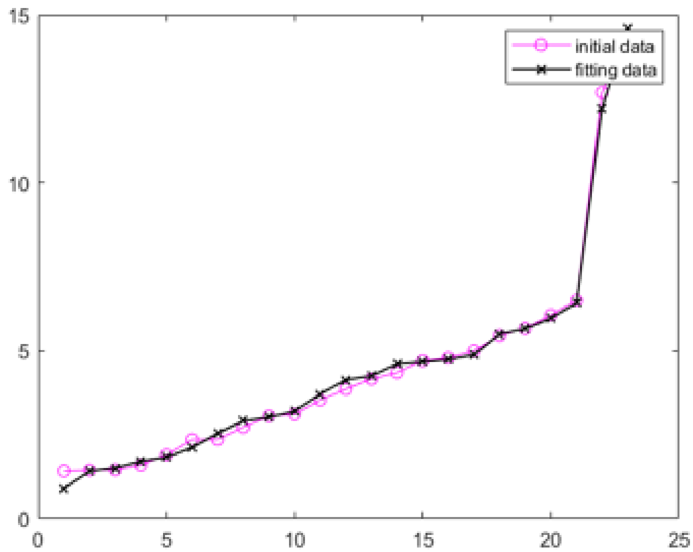

Figure 6. Fitted curves of barium oxide and silica (left).

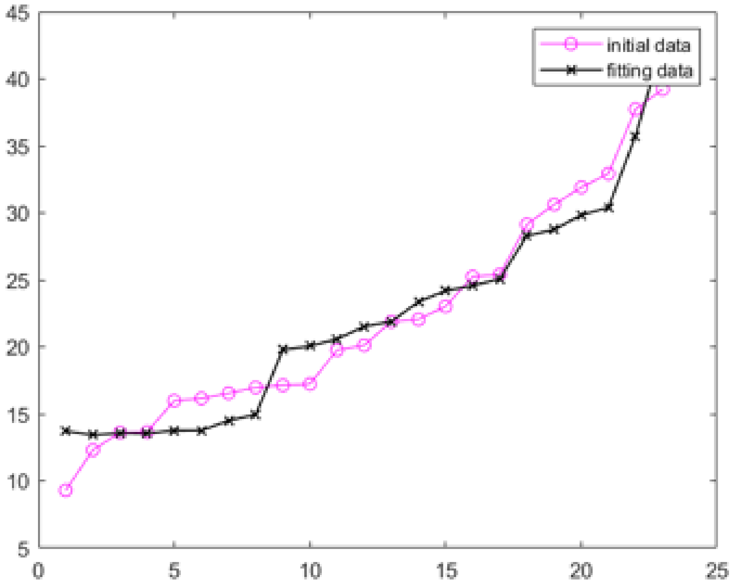

Figure 7. Fitted curves of strontium oxide and silica (right).

Table 4. Composition prediction of Pb barium glass before weathering.

sampling point	SiO_2	CaO	Al_2O_3	PbO	P_2O_5
02	65.16367	1.628012	0.304908	26.64657	0
08	35.93666	2.866246	16.40879	25.56215	7.203184
11	54.97847	2.522339	8.016505	27.41303	3.430924
19	53.26801	2.112176	3.650369	24.90611	1.904412
26	37.32358	3.097126	17.04139	26.11905	7.655632
34	43.37075	0.801521	4.950488	15.77157	1.454761
36	43.16718	0.42693	4.967766	14.38023	0.989138
38	48.02988	1.13192	5.057284	15.91993	1.868311
39	53.77176	2.028984	4.633658	17.98374	2.844649
40	55.7976	1.967469	4.294035	17.25725	2.661719
41	90.96239	2.464717	4.104902	40.70686	0
43point1	67.09476	4.212638	6.020961	32.96183	4.699362
42point2	66.53212	2.603963	2.722358	27.55382	1.705994
48	68.89108	1.309659	2.97706	28.49563	0
49	73.10756	2.298399	3.304257	30.51389	0.744724
50	58.98233	1.948583	7.302208	21.5997	2.80667
51point1	65.86839	1.958464	4.526293	27.87928	1.067219
51point2	64.74752	1.339574	0	28.60396	0
52	57.57862	1.578633	4.508494	21.38034	1.488707
54	79.56127	3.509757	4.783908	31.53587	2.878691
54Severe weathering	85.53041	4.943876	2.967043	33.73405	4.378422
56	36.01899	-0.60236	6.202208	12.15102	0.075036
57	35.14406	-0.61425	7.025587	12.32039	0.288611
58	56.53291	2.041946	4.436526	26.05206	1.741365
goodness of fit	0.86612	0.94539	0.996	0.93827	0.90281
spearman	0.8887	0.5269	-0.6601	0.8682	-0.5769

Table 5. Composition prediction of high potassium glass before weathering.

sampling point	SiO_2	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3
07	74.3123	11.5846	7.34660	1.54204	3.02792	8.41986
09	64.8400	7.42227	3.95274	0.77593	1.19028	5.62635
10	60.8605	5.67356	2.52692	0.45408	0.41825	4.45274
12	65.4005	7.66856	4.15356	0.82126	1.29902	5.79164
22	59.2351	4.95930	1.94454	0.32261	0.10292	3.97338
27	64.7839	7.39764	3.93266	0.77140	1.17941	5.60982
goodness of fit	0.89203	0.86702	0.87371	0.92871	0.88086	0.92781
spearman	0.8643	0.7932	0.7152	0.8977	0.6509	0.851

3. Modeling and solving of glass type identification

3.1. R type cluster analysis to verify the classification basis

By observing the frequency histogram [6] can be seen that high potassium and lead barium glass composition is the biggest difference between before and after weathering kali, 3 oxidation 2 aluminium and lead oxide proportion is different, so this article assumes that the several kinds of chemical substances as the key to distinguish high potassium and lead barium glass, this article use R type cluster [7] to the categorization of dividing basis for validation, draw 1,3,4,5,6,7,9, Cultural relics No. 10, 12, 13, 15, 16, 17, 18, 21, 22, 28, 30 belong to the high potassium category, and the rest belong to the lead and barium category. By comparing with Table 1, the classification results are almost the same, indicating that such classification is feasible, as shown in Figure 8.

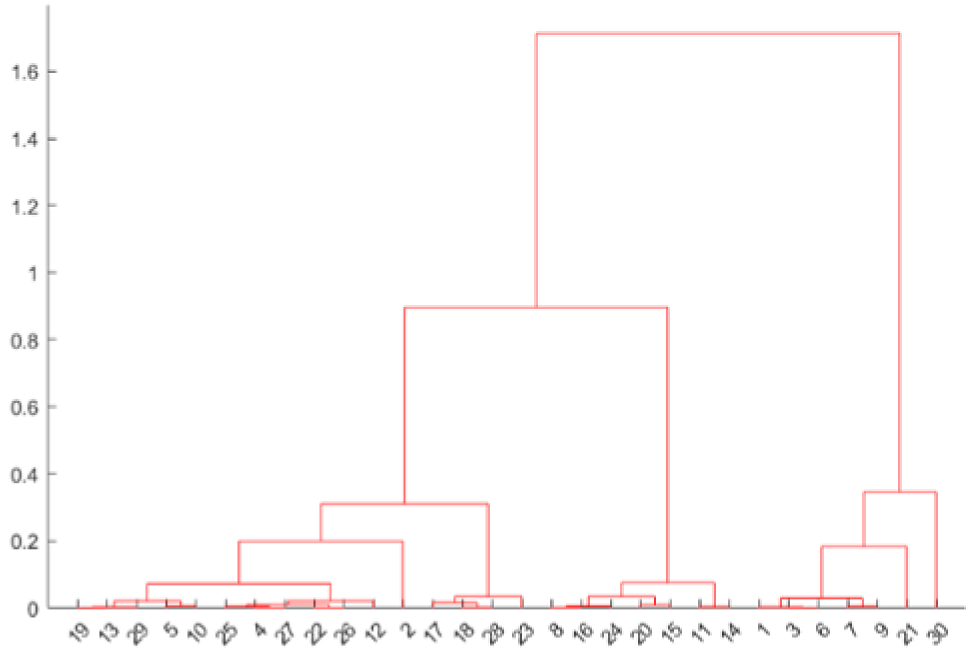

Figure 8. R-type clustering diagram.

3.2. R-type clustering method was used for subclass analysis, sensitivity and rationality test

The sensitivity test in this paper is based on R-type cluster analysis, which takes the first element of each category as the dependent variable and the rest as the independent variable to calculate its coefficient. The derivative value of its linear curve can be calculated by adding the coefficients, as shown in Figure 9. The larger the derivative value, the higher the sensitivity will be [8].

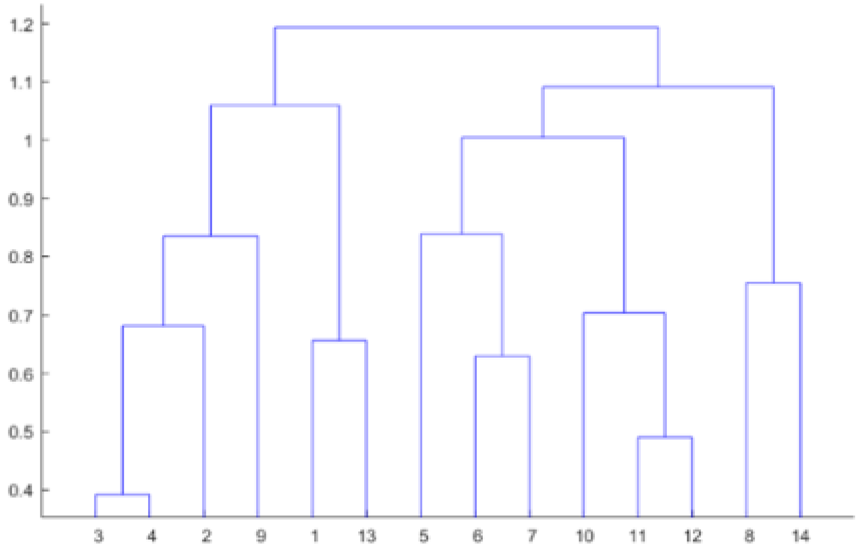

Figure 9. R-type clustering diagram of high potassium class.

Chemical elements were divided into subclasses by R-type clustering. Through multiple tests, it was found that chemical elements with high potassium content should be divided into three classes, which are respectively, as shown in Table 6.

Table 6. Subclass division of high potassium glass.

class	Element	Sensitive value
1	CuO,SO_2	3.4016
2	MgO,Al_2O_3,Fe_2O_3,BaO,P_2O_5,SrO	11.3879
3	SnO_2	-5.0563

Then, each element of each group was correlated with each other to verify the rationality, and the correlation value was calculated as shown in the following table.

0.842898	-0.50434	-0.86746	-0.82054	-0.3176	0.034654	0.611937	0.648084	0.503475	-0.11329	0.755372	0.150506	0.165347	0.343757	-0.28491	-0.12101
0.408793	0.698665	0.588969	0.50674	0.663407	0.734547	0.690828	0.518613	0.680202	0.636726	0.531648	0.780832	0.596119	0.621921	0.425764	

Most of them are relatively high, which proves that there is a greater correlation, so the classification is reasonable, as shown in Figure 10 and Table 7.

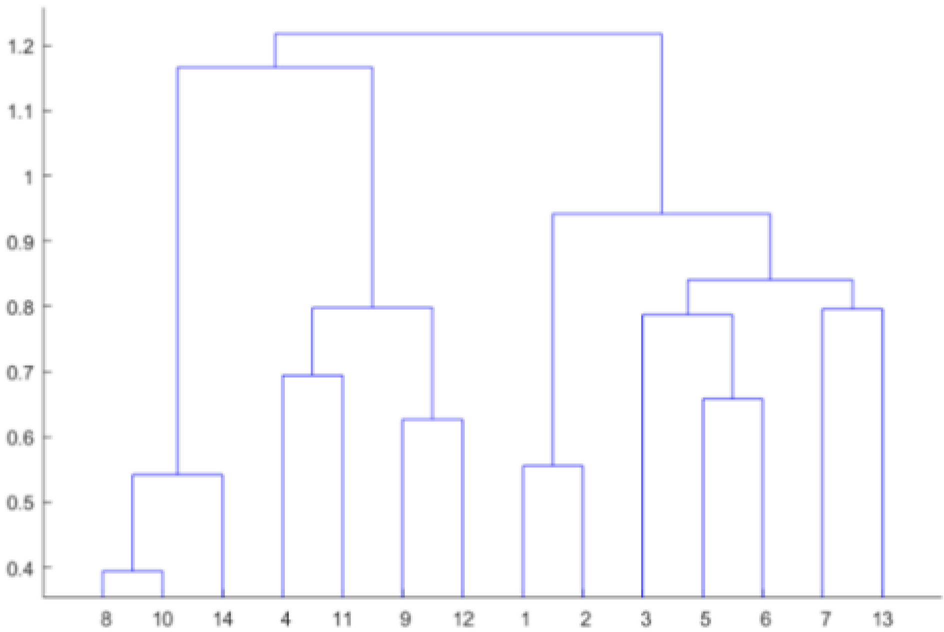

Figure 10. R-type clustering diagram of lead and barium.

Table 7. Subclass division of lead and barium glass.

class	Element	Sensitive value
1	SiO_2,Na_2O	3.3409
2	K_2O,MgO,Al_2O_3,Fe_2O_3,SnO_2	0.1702
3	CuO,BaO,SO_2	1.0606
4	CaO,PbO,P_2O_5,SrO	-0.2396

The elements of lead and barium fall into four categories, the correlation coefficients are shown in the table below. There is a large correlation, reasonable classification.

0.3505	0.2831	0.3173	0.4289	0.7916	0.5431	0.4592	0.3635	0.5240	0.1512	0.3428	0.4474	0.2563

4. Modeling and solving of chemical composition of glass

The correlation coefficient method was used to solve the problem: the correlation coefficients between the contents of pairwise chemical substances were calculated by using the forms of high potassium and lead and barium respectively, and two inverted triangular matrices were listed. The high potassium was shown in Table 8 [9]:

Table 8. Correlation coefficient of high potassium chemical content.

	SiO2	Na2O	K2O	CaO	MgO	Al2O3	FeO	CuO	PbO	BaO	P2O5	SrO	SnO	SO2
SiO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Na2O	-0.35483	0	0	0	0	0	0	0	0	0	0	0	0	0
K2O	-0.972188	0.6694545	0	0	0	0	0	0	0	0	0	0	0	0
CaO	-0.342748	1.0128239	0.6580321	0	0	0	0	0	0	0	0	0	0	0
MgO	-0.602939	-0.239101	0.0891426	-0.269537	0	0	0	0	0	0	0	0	0	0
Al2O3	-1.218032	0.2643464	0.2881528	0.3749149	0.26972	0	0	0	0	0	0	0	0	0
FeO	-0.712459	0.2536889	0.0597748	0.0318613	0.31724	0.48082	0	0	0	0	0	0	0	0
CuO	-0.068151	0.0501111	0.2897693	0.4909974	0.38906	0.48644	0.77035	0	0	0	0	0	0	0
PbO	0.4959975	0.8582337	0.2796672	-0.019761	0.16356	0.9366	0.15167	-0.0642	0	0	0	0	0	0
BaO	0.0485369	-0.202825	-0.09586	0.1947032	.91960614	0.81578	0.79375	-0.5185	0.55073	0	0	0	0	0
P2O5	0.0634783	0.1912748	0.3040199	-0.545754	0.3378	0.72318	0.59594	0.2059	-0.3174	0.77479	0	0	0	0
SrO	0.0020004	-0.076734	0.4827972	-0.182444	0.60436	0.76479	0.6629	-0.1958	-0.4976	0.35143	0.58657	0	0	0
SnO	-0.034139	-0.024209	-0.033112	-0.50455	0.03058	-0.6276	-0.434	-0.2031	0.00739	-0.0564	0.1339	0.3187	0	0
SO2	-0.365104	-0.077529	0.4438651	0.5764082	0.69809	0.31789	0.43127	-0.1543	-0.0608	-0.662	0.01179	-0.0279	-0.0436	0

Lead and barium ions are shown in Table 9:

Table 9. Correlation coefficient of lead and barium chemicals content.

	SiO2	Na2O	K2O	CaO	MgO	Al2O3	FeO	CuO	PbO	BaO	P2O5	SrO	SnO	SO2
SiO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Na2O	-0.504341	0	0	0	0	0	0	0	0	0	0	0	0	0
K2O	-0.867458	0.6119372	0	0	0	0	0	0	0	0	0	0	0	0
CaO	-0.820536	0.6480836	0.7553722	0	0	0	0	0	0	0	0	0	0	0
MgO	-0.597553	-0.2354858	0.3722724	0.1911263	0	0	0	0	0	0	0	0	0	0
Al2O3	-0.850716	0.3505008	0.60546268	0.5375286	0.62866	0	0	0	0	0	0	0	0	0
FeO	-0.683437	-0.009911	0.31578837	0.4467013	0.58897	0.69083	0	0	0	0	0	0	0	0
CuO	-0.402378	0.0345072	0.1350568	0.4047305	0.09793	0.22052	0.53718	0	0	0	0	0	0	0
PbO	-0.317601	0.5034745	0.150506	0.3437569	0.12494	0.48285	0.09913	-0.1456	0	0	0	0	0	0
BaO	-0.237427	-0.200141	-0.170938	-0.049076	0.50674	0.51861	0.53165	0.27313	0.40237	0	0	0	0	0
P2O5	-0.481487	-0.1940714	0.1974521	-o0.0217756	0.66341	0.6802	0.78083	0.28148	.02542978	0.62192	0	0	0	0
SrO	-0.476262	-0.152499	0.3491462	-0.031203	0.73455	0.63673	0.59612	-0.0186	0.05026	0.42576	0.8429	0	0	0
SnO	0.03.465431	-0.1132947	0.1653465	-0.284915	0.27013	-0.161	-0.214	-0.3813	-0.121	-0.1104	0.0611	0.2905	0	0
SO2	-0.400727	-0.20814	0.37998s35	0.4533458	0.42505	0.15168	0.24932	0.40879	-0.2223	-0.2028	-0.0282	-0.0048	-0.1148	0

Then find out the components with correlation coefficient greater than 0.6 that represent the greater correlation between elements.

High potassium glass is shown in the following table:

element	3	4	5	7	3	4	4	6	6	11	12	7	11	12	11	11	12
	1	1	1	1	2	2	3	3	5	5	5	6	6	6	7	10	11
corrcoef	-0.86746	-0.82054	-0.8502	-0.6834	0.61137	0.64808	0.75537	0.60547	0.69867	0.63407	0.73455	0.69083	0.680202	0.63673	0.780832	0.62192	0.8429

Elements 1-14 respectively represent silica (SiO2), sodium oxide (Na2O), potassium oxide (K2O), calcium oxide (CaO), magnesium oxide (MgO), alumina (Al2O3), iron oxide (Fe2O3), copper oxide (CuO), lead oxide (PbO), Barium oxide (BaO), phosphorus pentaoxide (P2O5), Strontium oxide (SrO), tin oxide (SnO2), sulfur dioxide (SO2) , as shown in Table 10.

Table 10. Lead and barium are:

Element	9	10
	1	8
corrcoef	-0.8136	0.791591

By making the difference between the correlation coefficient of high potassium and the correlation coefficient of lead and barium, two chemical substances with great correlation difference were calculated. The larger the absolute value of the difference, the greater the difference. In this paper, if the absolute value of the difference is greater than 0.7, there is a great difference between them. It can be concluded that these related elements have great differences in different glass types.

5. Conclusion

Cultural relics data are relatively limited, linear regression with good performance on small data sets can well reflect the statistical law of data [10]. It is suitable for use in the case of some predefined variables and a simple prediction model; The prediction speed is fast; The results are interpretable and easy to state; In this paper, multiple linear regression analysis is written as a function, which is easy to update the model when new data is added. No parameter adjustment is required; No feature scaling is required.

To study the internal structure of correlation coefficient matrix of variables, find out a few random variables that can control all variables to describe the correlation between multiple random variables. Then the variables are grouped according to the magnitude of the correlation, so that the correlation between variables in the same group is high, and the correlation between variables in different groups is low. Can understand the relationship between individual variables, but also can understand the relationship between various variables. According to the classification results of variables and the relationship between them, the main variables can be selected for regression analysis. On the basis of known specific classification criteria, the model can be directly used to obtain accurate classification through certain data.

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