Composition analysis and identification of ancient glass products

Qun Wu[#], Congrong Xu[#], Bo Xiang[#]

School of Aeronautics and Astronautics, Shenyang Aerospace University, Shenyang, 110136, China
[#]These authors contributed equally

Abstract: High-potassium glass and lead-barium glass were two kinds of glass commonly used in ancient China. However, due to their susceptibility to weathering in the process of burial, their chemical composition content has changed, so it is necessary to explore and analyze. We first deleted the invalid data, and used Excel to make statistics on each decoration, type and color. Then we found that lead-barium glass was more likely to be weathered. Without considering the number of samples, B decoration was more likely to be weathered, and the relationship between color and weathering was not strong. Finally, under the condition of fixed glass types, Excel was used to calculate and visualize the chemical content changes of the main components before and after weathering. At the same time, tables were listed according to the obtained statistical rules, and the chemical composition content before and after weathering was compared to predict the chemical composition content before and after weathering.

1. Introduction

Also is the ancient glass, buried in different regions, raw materials, process, conditions and so on many factors, its main component will have a huge difference, how to use certain known conditions and the limited sample testing data to establish a reliable model, analysis and identification of the unknown glass has very important meaning and value.

In this paper, we first need to obtain the relationship between the surface weathering of glass relics and their glass types, ornamentations and colors through statistical processing of known data. Second, taking high potassium and lead-barium glass as the first classification factor, and surface weathering as the second classification factor, the relationship between weathering and chemical composition content was analyzed according to the proportion of the corresponding main components in the test samples given in the known data. Finally, according to the obtained relationship and weathering point detection data, the chemical composition content before weathering was predicted[1].

2. Data preprocessing

Firstly, Excel was used to process the known data: screening and classifying according to the

decoration, glass type, color and surface weathering, and counting the number and proportion of samples. Three cluster bar graphs were established to directly reflect the relationship in the first requirement, which was convenient for analysis[2].

Since the cultural relics sampling points of known data are random samples on the surface of corresponding numbered cultural relics in known data, the remaining 67 groups of valid sample data can be divided into four categories for analysis by weathering conditions and glass types: high-potassium glass not weathered, high-potassium glass weathered, lead-barium glass not weathered, and lead-barium glass weathered[3].The second requirement can be met according to the differences in the proportions of each component in different categories. Based on the above analysis, it can be concluded that the typical multi-component components such as silica and lead oxide of glass cultural relics samples are significantly different before and after weathering. Therefore, the chemical composition content before weathering can be predicted based on this rule and the data detected at weathering points. The relationship between weathering and other variables is shown in Figure 1.
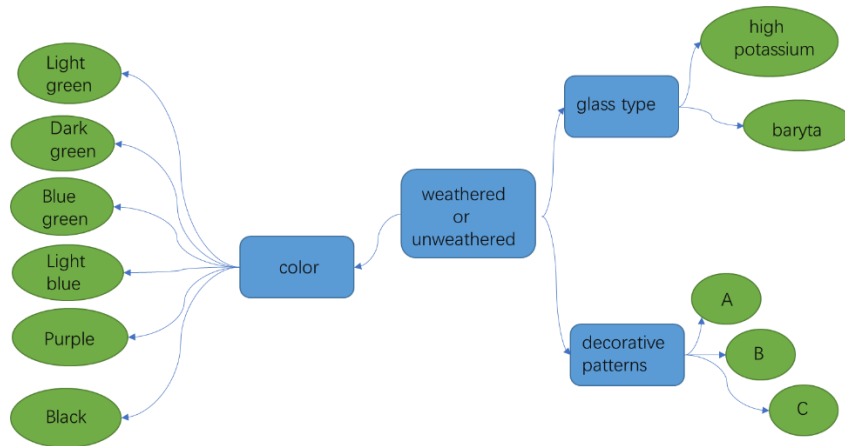

Figure 1: Relationship between weathering and other variables

According to the above analysis, after statistical and comprehensive analysis of the data, it is easy to obtain the tufted bar chart that reflects the relationship between surface weathering of glass cultural relics and their glass types, ornamentations and colors, respectively, as shown in Figure 2[4].
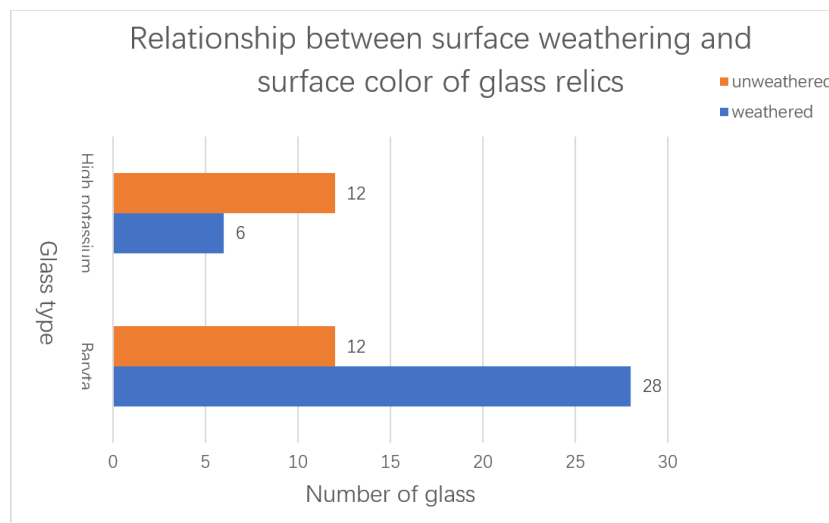

Figure 2: Statistical chart of surface weathering and glass types of glass cultural relics

According to the simple formula, it can be calculated as follows:

$$F = \frac{q}{m} \times 100\% \qquad (1)$$

F is the weathering rate, q representing the number of weathered glass relics in each category, m representing the total number of glass relics.

Figure 2 shows that among 58 glass relics, the weathering rate of high-potassium glass is 33.4%. The weathering rate of lead-barium glass is 70.0%, which is much higher than that of high-potassium glass relics. Lead-barium glass is more likely to be weathered, while high-potassium glass is not[5].
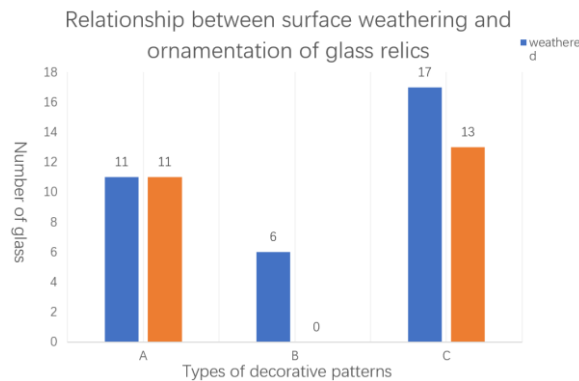

Figure 3: Statistical chart of surface weathering and ornamentation of glass cultural relics

Figure 3 shows that among 58 glass relics, the weathering rate of A decoration sample is 50.0%, and there is no obvious inevitable relationship between A decoration and weathering. All 6 samples of B decoration are weathered, so it can be considered that B decoration is easy to cause glass weathering without considering the number of samples and the reliability of the test structure. The weathering rate of C decoration was 56.7% in 30 samples. It can be speculated that C decoration may be conducive to weathering, but the effect is not as significant as B decoration. In contrast, it can be considered that glass relics with ornamentation A and C are not easily weathered [6].
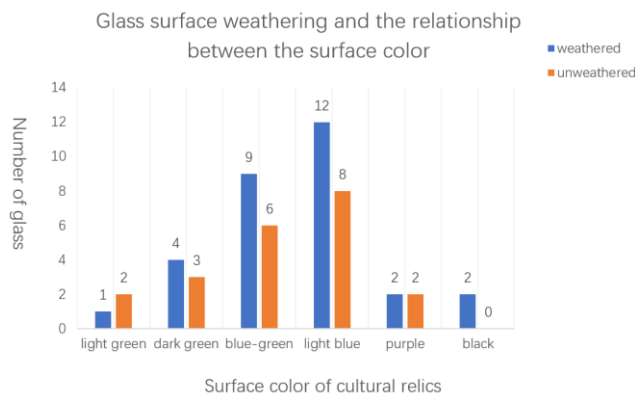

Figure 4: Surface weathering and surface color statistics of glass relics

It can be seen from Figure 4 that among the collected glass cultural relics, dark green, blue-green and light blue samples accounted for more, and the number of weathered samples was higher than that of unweathered ones. The weathering rates were dark green: 57.1%;Blue-green: 60.0%;Light blue: 60.0%;The samples with light green, purple and black colors accounted for less of the total samples, and there was no significant difference in weathering[7]. Therefore, we can think that the color of glass relics was near the transition range from green to blue, and its surface weathering

degree was higher. In this problem, the color can be seen as a glass, coating material elements of cultural relics and environmental elements such as a characteristic of many factor combined action result, as to what color corresponds to the surface of the cultural relics of the weathering rate is highest, and the more light green, purple, black, or color effect still need more sample size and quantity to determine, so this article will not get this problem.

3. Composition and content analysis

To analyze the relationship between surface weathering and composition content of glass cultural relics samples, firstly, samples in the known data are divided into four groups by comprehensively considering the type and whether the glass is weathered. The groups and sample sizes are shown in Table 1[8].

Table 1: A grouping of glass types and weathering conditions

Set no.	group	Sample size (group)
1.	No weathering of lead-barium glass	23
2.	Lead-barium glass weathering	26
3.	High potassium glass has no weathering	12
4.	High potassium glass weathering	6

Because each group contains more samples and data, we first calculated the average and variance of the chemical composition content of each group to extract representative data of each category.

$$SUM_j = \sum_{i=1}^{n} X_j \tag{2}$$

SUM_j is the algebraic sum of the JTH chemical composition proportion of n groups of samples in the current class.

$$A_j = \frac{1}{n} SUM_j \tag{3}$$

A_j is the arithmetic average proportion of the JTH chemical component of the total n groups of samples in the current class.

$$S_j = \sqrt{\frac{1}{n}[\sum (X_{ij} - A_j)^2]} \tag{4}$$

S_j is the standard deviation value of the JTH chemical component of the total n group samples of the current class[9].

Table 2: Differences in the mean values of each content between weathered and unweathered glasses

	SiO$_2$	Na$_2$O	K2O	CaO	MgO	Al2O3	Fe2O3	CuO	PbO	BaO	P2O5	SrO	SnO2	SO2
Lead barium glass														
unweathered	54. 66	1. 68	0. 22	1. 32	0. 64	4. 46	0. 74	1. 43	22. 08	9. 00	1. 05	0. 27	0. 05	0. 16
standard deviation	11. 33	2. 27	0. 30	1. 23	0. 52	3. 12	1. 11	1. 89	8. 03	5. 70	1. 81	0. 24	0. 12	0. 75
weathering	23. 78	0. 19	0. 13	2. 69	0. 61	2. 54	0. 57	2. 37	44. 42	11. 99	5. 44	0. 43	0. 02	1. 42
standard deviation	8. 71	0. 53	0. 23	1. 63	0. 67	1. 45	0. 72	2. 73	10. 86	9. 94	4. 11	0. 26	0. 09	4. 20
Change the amount	-30.88	-1.49	-0.09	1.37	-0.03	-1.91	-0.17	0.94	22.33	2.99	4.40	0.16	-0.03	1.26
High potassium glass														
unweathered	67. 98	0. 70	9. 33	5. 33	1. 08	6. 62	1. 93	2. 45	0. 41	0. 60	1. 40	0. 04	0. 20	0. 10
standard deviation	8. 38	1. 23	3. 75	2. 96	0. 65	2. 39	1. 60	1. 59	0. 56	0. 94	1. 37	0. 05	0. 65	0. 18
weathering	93. 96	0. 00	0. 54	0. 87	0. 20	1. 93	0. 27	1. 56	0. 00	0. 00	0. 28	0. 00	0. 00	0. 00
standard deviation	1. 58	0. 00	0. 41	0. 45	0. 28	0. 88	0. 06	0. 85	0. 00	0. 00	0. 19	0. 00	0. 00	0. 00
Change the amount	67.98	0.70	9.33	5.33	1.08	6.62	1.93	2.45	0.41	0.60	1.40	0.04	0.20	0.10

According to the content of the main components involved, we divided them into many elements and few elements (different from the large elements and trace elements in chemical terms). For example, silicon dioxide and lead oxide in Table 2 are typical of many elements, and those with less than 5% are typical of few elements.

By calculation, as shown in Table 2 above, comparing group ① with group ②, it is easy to find that for lead-barium glass, the content of silica in weathered samples is significantly reduced, with an average reduction of about 30.88 percentage points, and the content of lead oxide is also significantly increased, with an average increase of about 22.33 percentage points.For high-potassium glass, the content of silica in the samples after weathering increased significantly, with an average increase of about 25.98 percentage points. However, different from lead-barium glass, lead oxide is a small element in high-potassium glass, and its content is not significantly different before and after weathering, and is almost zero.In addition, the content of potassium oxide decreased significantly after weathering, with an average value of 8.79 percentage points[10].

It is worth noting that the main elements of lead-barium glass increased and decreased after weathering, while the content of other elements in high-potassium glass decreased except for silica.

Next, the values were statistically analyzed and the compound scatter plots of chemical composition contents corresponding to the following four groups were drawn, and the images of the two groups of chemical compositions with significant changes were analyzed.
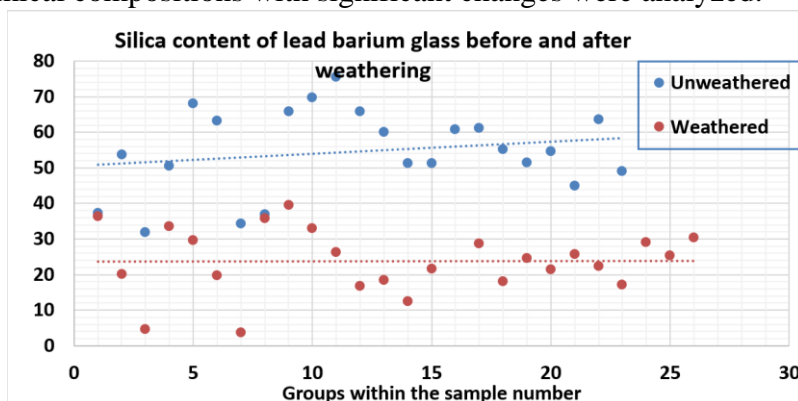

Figure 5: Comparison of SiO before and after weathering in groups ① and ② of lead-barium glass2Content of the figure

Figure 5 shows the comparison of silica content before and after weathering of lead-barium glass. It is obvious that silica content decreased significantly. The silica content before weathering is about 50% to 70%, and the silica content after weathering is about 10% to 30%, showing obvious effect.
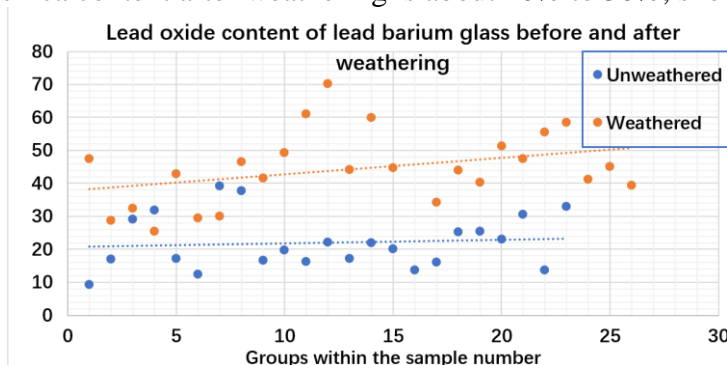

Figure 6: PbO content of PB-barium glass before and after weathering compared with group ① and group ②

Figure 6 shows that the content of lead oxide increased significantly after weathering of lead-barium glass. The concentration of lead dioxide in lead-barium glass before and after weathering is obviously concentrated, and the typical statistical law of chemical composition content and weathering condition of lead-barium glass can be more intuitively reflected when combined with Figure 8.
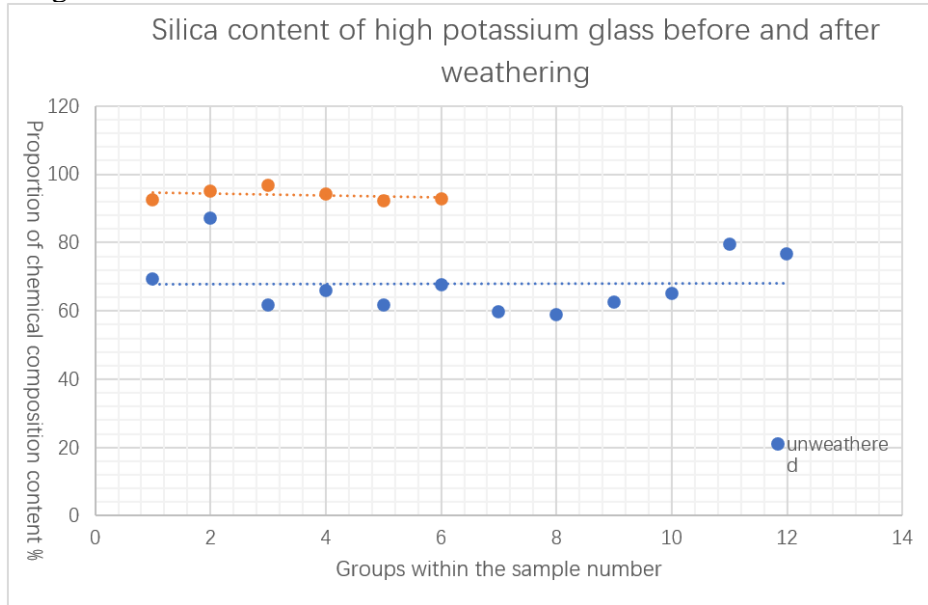

Figure 7: Comparison of SiO2 content of lead-barium glass before and after weathering in groups ③ and ④

Figure 7 shows that the silica content of high-potassium glass increases significantly after weathering, and the distribution is concentrated. Although the samples are small, we can still see that there is a significant difference between before and after weathering. The pre-weathering content is about 90%-100%, and the post-weathering content is mainly in the region of 60%-80%.
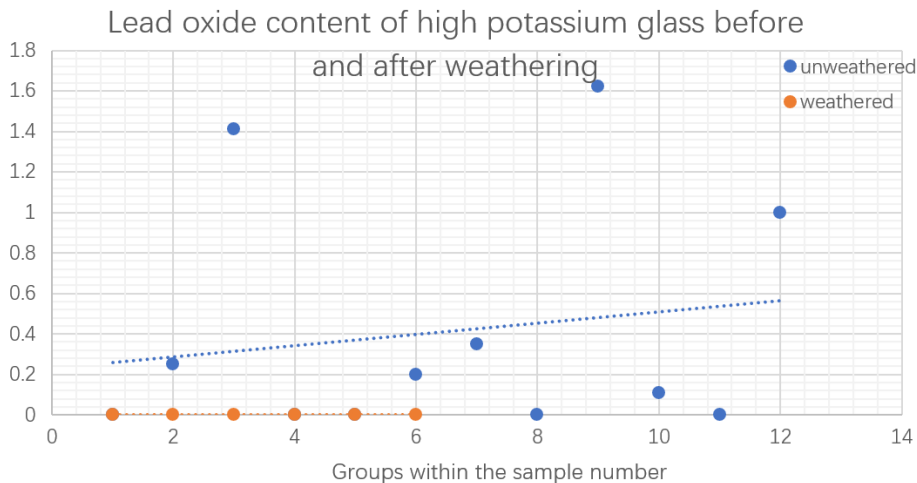

Figure 8: PbO content of PB-barium glass before and after weathering compared with groups ③ and ④

Figure 8 shows that the content of PBO in high-potassium glass decreases significantly after weathering, and the content of PBO in six weathered samples decreases to 0. Compared with Figure 7, the typical statistical law of chemical composition content and weathering status of

high-potassium glass samples can also be more intuitively reflected.

4. Pre-weathering content prediction

Next, we predicted the chemical composition content before weathering according to the detection data of weathering points. Therefore, on the basis of the above problems, we used data statistical analysis method to calculate the average content of main chemical components for lead-barium glass and high-potassium glass under different wind conditions, and then calculated the variation amount of each component one by one through the changes of unweathered and weathered contents in the same glass cultural relics. The results are shown in Table 3.

Table 3: Prediction model of chemical composition content before weathering based on statistical analysis

	SiO$_2$	Na$_2$O	K2O	CaO	MgO	Al2O3	Fe2O3	CuO	PbO	BaO	P2O5	SrO	SnO2	SO2
						Lead barium glass								
unweathered	54. 66	1. 68	0. 22	1. 32	0. 64	4. 46	0. 74	1. 43	22. 08	9. 00	1. 05	0. 27	0. 05	0. 16
standard deviation	11. 33	2. 27	0. 30	1. 23	0. 52	3. 12	1. 11	1. 89	8. 03	5. 70	1. 81	0. 24	0. 12	0. 75
weathering	23. 78	0. 19	0. 13	2. 69	0. 61	2. 54	0. 57	2. 37	44. 42	11. 99	5. 44	0. 43	0. 02	1. 42
standard deviation	8. 71	0. 53	0. 23	1. 63	0. 67	1. 45	0. 72	2. 73	10. 86	9. 94	4. 11	0. 26	0. 09	4. 20
Change the amount	-30.88	-1.49	-0.09	1.37	-0.03	-1.91	-0.17	0.94	22.33	2.99	4.40	0.16	-0.03	1.26
After test	X1	X2	X3	X4	X5	X6	X7	X8	X9	X10	X11	X12	X13	X14
before predict	X1+30.88	X2-1.49	X3+0.09	X4-1.37	X5+0.03	X6+1.91	X7+0.17	X8-0.94	X9-22.33	X10-2.99	X11-4.4	X12-0.16	X13+0.03	X14-1.26
						High potassium glass								
unweathered	67. 98	0. 70	9. 33	5. 33	1. 08	6. 62	1. 93	2. 45	0. 41	0. 60	1. 40	0. 04	0. 20	0. 10
standard deviation	8. 38	1. 23	3. 75	2. 96	0. 65	2. 39	1. 60	1. 59	0. 56	0. 94	1. 37	0. 05	0. 65	0. 18
weathering	93. 96	0. 00	0. 54	0. 87	0. 20	1. 93	0. 27	1. 56	0. 00	0. 00	0. 28	0. 00	0. 00	0. 00
standard deviation	1. 58	0. 00	0. 41	0. 45	0. 28	0. 88	0. 06	0. 85	0. 00	0. 00	0. 19	0. 00	0. 00	0. 00
Change the amount	25.98	-0.70	-8.79	-4.46	-0.88	-4.69	-1.67	-0.89	-0.41	-0.60	-1.12	-0.04	-0.20	-0.10
After test	X1	X2	X3	X4	X5	X6	X7	X8	X9	X10	X11	X12	X13	X14
before predict	X1-25.98	X2+0.7	X3+8.79	X4+4.46	X5+0.88	X6+0.88	X7+1.67	X8+0.89	X9+0.41	X10+0.6	X11+1.12	X12+0.04	X13+0.2	X14+0.1

When the data of weathering samples are known, the pre-weathering chemical content can be predicted by comparing the red and blue parts of FIG. 8. Among them, X1 to X14 correspond to the contents of 14 chemical components involved in the weathered samples respectively, and the prediction can be achieved by looking up the table.In addition to the difference in average content, the accuracy of the prediction can be judged by the standard deviation of the known content mean of different weathering states. The effect of weathering on the small amount of elements in potassium glass is far less than that of the large amount of elements, which is consistent with the prediction results obtained in this question.

5. Conclusion

High-potassium glass and lead-barium glass were two types of glass commonly used in ancient China.However, due to their susceptibility to weathering in the process of burial, their chemical composition content changed, so it is necessary to explore and analyze.We first deleted the invalid data, and used Excel to make statistics on each decoration, type and color. Then we found that lead-barium glass was more likely to be weathered. Without considering the number of samples, B decoration was more likely to be weathered, and the relationship between color and weathering was not strong.Finally, under the condition of fixed glass types, Excel was used to calculate and visualize the chemical content changes of the main components before and after weathering.At the same time, tables were listed according to the obtained statistical rules, and the chemical composition content before and after weathering was compared to predict the chemical composition content before and after weathering.

References

[1] Frabasil Joaquin, Rivas Dana Velasquez, Bertot Gustavo M., Gualco Luciana, Ricardo Carabajal, Carozza Patricia, Gaggioli Daniela, Colmenares Gabriela, Sokn Silvia. Correlation analysis between lysosomal enzyme activities and the different types of leukocytes in dried blood spots [J]. Molecular Genetics and Metabolism, 2022, 135(2).

[2] Lu Yier, Ye Chenyang, Yuan Ying. Phenotypic characteristics and T cell receptor properties in melanoma: deciphering the correlation at single-cell resolution [J]. Signal Transduction and Targeted Therapy, 2022,7(1).

[3] G.E. X, Zhou A, Chen J. POSB261 Cancer Patients' Willingness to Pay per Quality-Adjusted Life Year in ASIA-Pacific: A Systematic Review and Correlation Analysis with Population Metrics [J]. Value in Health, 2022, 25(1S).

[4] Weir Bruce S, Anderson Amy D, Hepler Amanda B. Author Correction: Genetic relatedness analysis: modern data and new challenges.[J]. Nature reviews. Genetics,2021,23(2).

[5] Luo Shiqiang, Chen Xingyuan, Zeng Dingyuan, Tang Ning, Yuan Dejian, Zhong Qingyan, Mao Aiping, Xu Ruofan, Yan Tizhen. Correction to: The value of single-molecule real-time technology in the diagnosis of rare thalassemia variants and analysis of phenotype-genotype correlation.[J]. Journal of human genetics,2021, 23(6).

[6] Shutaywi Meshal, Kachouie Nezamoddin N.. Silhouette Analysis for Performance Evaluation in Machine Learning with Applications to Clustering [J]. Entropy,2021,23(6).

[7] Poerwanto B. Evaluating the K-Means Analysis in Clustering Area Based on Estates Productivity in Tana Luwu Using Silhouette Index [J]. Journal of Physics: Conference Series, 2021, 1752(1).

[8] Dinesh Kumar Yadav, Rati Shukla, Vikash Yadav. An efficient collaborative recommender system for textbooks using silhouette index and K-means clustering technique [J]. International Journal of Advanced Intelligence Paradigms, 2021, 19(2).

[9] N. Nidheesh, K. A. Abdul Nazeer,P. M. Ameer. A Hierarchical Clustering algorithm based on Silhouette Index for cancer subtype discovery from genomic data [J]. Neural Computing and Applications, 2019, 32(15).

[10] Xu Wang, Yusheng Xu. An improved index for clustering validation based on Silhouette index and Calinski-Harabasz index [J]. IOP Conference Series: Materials Science and Engineering, 2019, 569(5).