Composition Analysis and Identification of Ancient Glass Products

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Abstract. Ancient glass products are valuable evidences for studying the cultural exchanges between China and the West in ancient times. Because ancient glass is easily weathered by the influence of burial environment, its chemical composition changes, which affects the correct judgment of glass types. This paper mainly makes full use of the known sample data through the establishment of statistical models, classification models, correlation analysis models, and the combination of numbers and shapes, The important indexes affecting surface weathering are studied respectively; The chemical composition law, classification, correlation and difference of glass cultural relics have been established, and a high accuracy identification model of glass cultural relics has been established, which is of great significance to the identification of glass cultural relics.

Keywords: Spearman Correlation Coefficient, Grey Correlation Analysis, Principal Component Analysis.

1. Introduction

The appearance of ancient Chinese glass is similar to that of foreign glass products, but the chemical composition is different. The glass variety invented by our country is the lead barium glass with high content of lead oxide (PbO) and barium oxide (BaO) as the main lead ore as the flux. Potassium glass is popular in Lingnan, Southeast Asia, India and other regions in China. It is fired with materials with high potassium content as flux. In the weathering process, the chemical composition of ancient glass will exchange with the chemical elements in the environment, making its composition ratio change. Based on the effective datas of the proportion of the main components of weathered cultural relics, the model of category and chemical composition is established to compare the relationship between different categories of chemical composition [1-2].

The relationship between the surface weathering of glass relics and their glass types, patterns and colors can be analyzed through the correlation between indicators. Spearman can be used to analyze this problem; For the analysis of the chemical formation law of the surface of cultural relics, statistical knowledge needs to be used for statistical law analysis to obtain the mean value, variance and other data [3].

In order to predict the chemical composition of glass relics before weathering, due to the difference between high potassium glass and lead barium glass, it is necessary to predict separately. According to the knowledge of chemistry, the chemical composition of weathered glass relics before weathering is similar to that of weathered glass relics. Therefore, the chemical content of weathered glass relics before weathering can be transferred to the chemical composition before weathering. Since the number of samples is small after classifying the glass relics, Booststrap is used to analyze the samples before weathering. Because Booststrap requires samples to obey normal distribution, it is necessary to conduct normal distribution test through JB normal distribution test and sample data before analysis [4].

In order to analyze the relationship between the chemical components of high potassium glass and lead barium glass, principal component analysis can be used to analyze them. The category of the principal components is the relationship between the chemical components. Then, through the grey correlation analysis, the quantitative correlation degree of chemical components can be obtained. By comparing the correlation degree between different types of chemical components, the difference of the correlation relationship of chemical components can be obtained [5].

2. Influence factors of glass surface weathering and chemical composition analysis before and after weathering

2.1. Correlation analysis

Spearman correlation coefficient can be used to describe the degree of correlation between data, and quantify the decoration, type, color and surface weathering through Excel.

Quantify the decoration:

$$W_i=\begin{cases}1,\ a_i=A\\2,\ a_i=B\\3,\ a_i=C\end{cases} \tag{1}$$

Where, a_i represents the decoration type of the cultural relics (A, B, C), i=1, 2, 3... 58.

Quantify the types of cultural relics:

$$\mathrm{L_i}=\begin{cases}0,\ \mathrm{b_i}=\text{Hyperkalemia}\\1,\ \mathrm{b_i}=\text{Lead barium}\end{cases} \tag{2}$$

Where, b_i represents the type of cultural relics (high potassium, lead barium), i=1, 2, 3... 58.

The collection for quantifying the color of cultural relics is as follows:

$$\text{Color}=\{0, 1, 2, 3, 4, 5, 6, 7\} \tag{3}$$

$$\mathrm{Q_i}=\begin{cases}0,\ \mathrm{c_i}=\text{Weathered}\\1,\ \mathrm{c_i}=\text{Unweathered}\end{cases} \tag{4}$$

Import the quantized data into SPSS software to obtain the following correlation coefficient table:

Table 1. Correlation coefficient table
***P>0.01 **P>0.0 *P>0.1

	Ornamentation	Type	color
Surface weathering	-0.0372	-0.3400**	0.1162

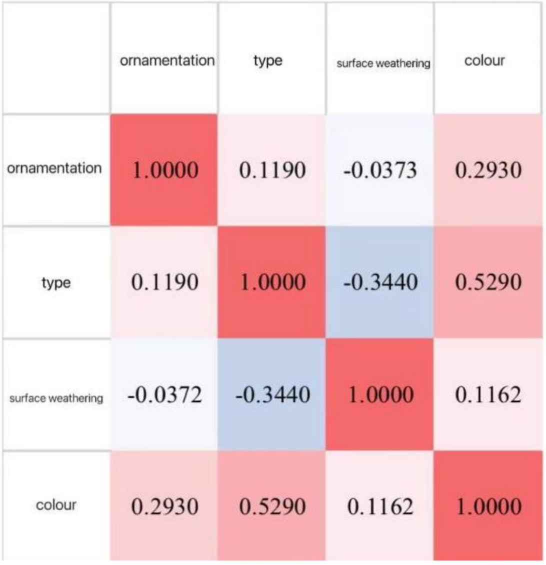

Figure 1. Color scale diagram of correlation coefficient

According to Table 6-1-1, the Spearman correlation coefficient between surface weathering and glass type is -0.344, and it passes the significance test at 0.01 level. The correlation coefficient is negative, indicating that the weathering degree is negatively related to the glass type, that is, high potassium glass is more susceptible to weathering. The Spearman correlation coefficient between surface weathering and ornamentation was -0.0373, which failed the significance test; The Spearman correlation coefficient between surface weathering and color was 0.1162, which also failed the significance test. It shows that there is no significant difference between surface weathering and these two variables. It can be concluded that the type of glass relics is an important factor affecting weathering.

The data are divided into two categories according to weathering and non-weathering, and their statistical laws are analyzed respectively. The p value calculated by the corr() function of matlab is shown in Table 2.

Table 2. Spearman coefficient significance test
***P>0.01 **P>0.0 *P>0.1

	Ornamentation	Type	color
Surface weathering	0.1894***	0.3960***	0.1346***

2.2. Statistical law analysis

After data preprocessing through Excel, the results of descriptive statistics on weathered and weathered lead barium glass and weathered and unweathered high potassium glass are shown in Table 3.

Table 3. Descriptive statistics of non-weathering chemical composition of lead barium glass

	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3
Maximum	31.94	0	0	0	0	1.44	0
Minimum value	87.05	4.66	14.52	8.7	1.98	11.15	6.04
Mean value	60.4232	0.7348	4.6132	3.2	0.774	4.8388	1.4124
Median	61.71	0	0.71	1.6	0.74	4.35	1
Skewness	-0.5005	1.5446	0.5279	0.4957	0.2344	0.798	1.1542
Kurtosis	2.8192	3.9598	1.5864	1.6572	1.78	3.017	4.0062
Standard deviation	14.0177	1.3942	5.3407	3.1334	0.6692	2.6183	1.6052

2.3. Qualitative analysis of chemical composition content

In the above figure, the black line represents weathered SiO_2, the blue line represents the unweathered SiO_2. The mean value of 2. The red scattered dots represent the weathered SiO_2, the green scattered dots represent the unweathered SiO_2. It is easy to know that after weathering, SiO_2 The average value of 2 decreases generally, but its proportion in the total composition increases. It can be seen from chemical knowledge that in nature, SiO_2 is the main component of Si, so the chemical composition change of weathered and unweathered glass is related to SiO_2 is weak. It can be speculated that before differentiation, glass relics contain SiO_2.

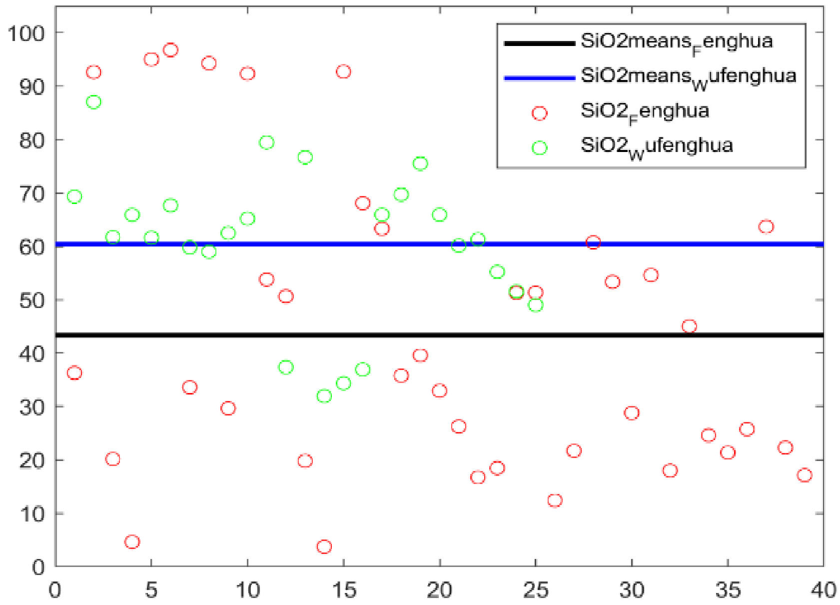

Figure 2. Composition Distribution Map of Weathered and Unweathered SiO_2

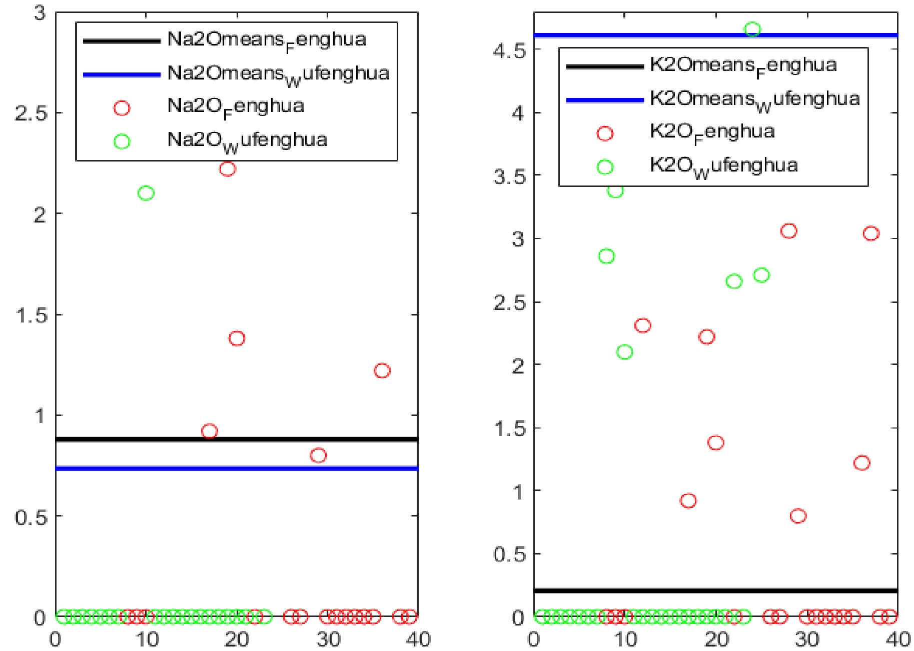

Figure 3. Composition Distribution Map of Weathered and Unweathered Na_2O and K_2O

In the above figure (left), the black line represents the mean value of Na_2O after weathering, the blue line represents the mean value of Na_2O before weathering, the red scatter represents the distribution of Na_2O after weathering, and the green scatter represents the distribution of Na_2O before weathering, and its proportion in the main component has also increased. It is easy to know that the mean value of Na_2O after weathering has increased, but the content of Na_2O in glass is low. From chemical knowledge, the structure of Na_2O is stable, Therefore, the change of chemical composition of weathered and fresh glass has a weak relationship with Na_2O. It can be inferred that there is Na_2O after weathering, and it can be inferred that there is also Na_2O before weathering, and the different proportions are mainly due to other increases or decreases.

In the above figure (right), the black line represents the mean value of K_2O after weathering, the blue line represents the mean value of K_2O before weathering, the red scatter represents the distribution of K_2O after weathering, and the green scatter represents the distribution of K_2O before weathering, and its proportion in the principal component has also increased. It is easy to know that the total mean value of K_2O after weathering decreases, but the content of K_2O in glass is low. From chemical knowledge, the structure of K_2O is unstable, Therefore, the change of chemical composition of weathered and fresh glass is strongly related to K_2O. It can be inferred that there is K_2O after weathering, and it can be inferred that the probability of K_2O before weathering is low.

Based on the analysis of the chemical composition distribution map and the stability of the compound, and the content of the chemical composition of the glass is related to the properties of the cosolvent, the comprehensive analysis shows that the qualitative relationship of the chemical composition before and after weathering is shown in Figure 4.

It can be seen from Figure 4 that if there are 9 chemical components in the left pie chart after weathering, they also exist before weathering, while if there are 5 substances in the right pie chart before weathering, they do not necessarily exist after weathering.

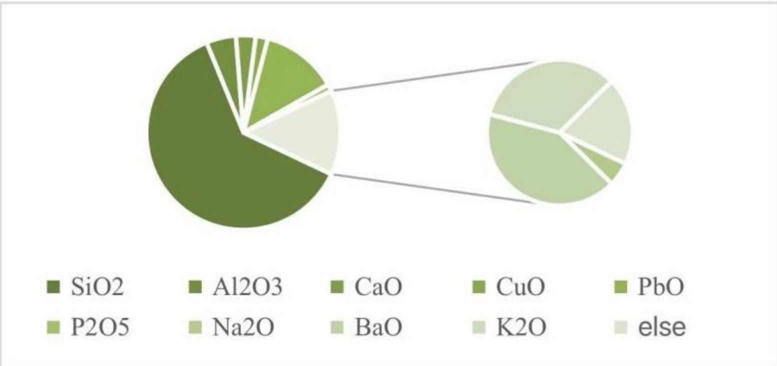

Figure 4. Chemical composition prediction table

2.4. Quantitative analysis of chemical composition content

Through the Bootstrap resampling simulation of sample data, the representative value of the newly formed sample set after a large number of samples can be estimated, and the standard deviation and confidence interval of the estimated value and other statistical parameters are given. Bootstrap resampling theory holds that the numerical distribution of the bootstrap resampled samples conforms to the distribution pattern of the sample population, and the mean value and standard deviation of the bootstrap sample numerical distribution are consistent with the sample population. Therefore, the mean value and standard deviation of the bootstrap resampled sample distribution conforming to the normal distribution can be used as a robust estimate of the representative values of limited single samples. Bootstrap is used to conduct multiple simulated repeated sampling of the data. On the basis of simulating a large number of samples from the original data sample set, a robust representative value estimation and standard deviation of fresh glass are obtained.

Table 4. JB inspection results

Chemical composition	h	Value of P	Chemical composition	h	Value of P
SiO_2	0	0.0842	CuO	0	0.5000
Na_2O	0	0.0381	PbO	0	
K_2O	0	0.0637	BaO	0	0.0499
CaO	0	0.1408	P_2O_5	0	0.0377
MgO	0	0.3734	SrO	0	0.0233
Al_2O_3	0	0.5000	SnO_2	1	0.0010
Fe_2O_3	0	0.0531	SO_2	0	0.0010

It can be seen from the above table that 99% of our confidence level accepts the original hypothesis.

Call the built-in function of matlab to check. After checking the unweathered lead barium glass, the data of the unweathered high potassium glass conform to the normal distribution. The normal fitting frequency histogram is obtained through MATLAB, as shown in Figure 5.

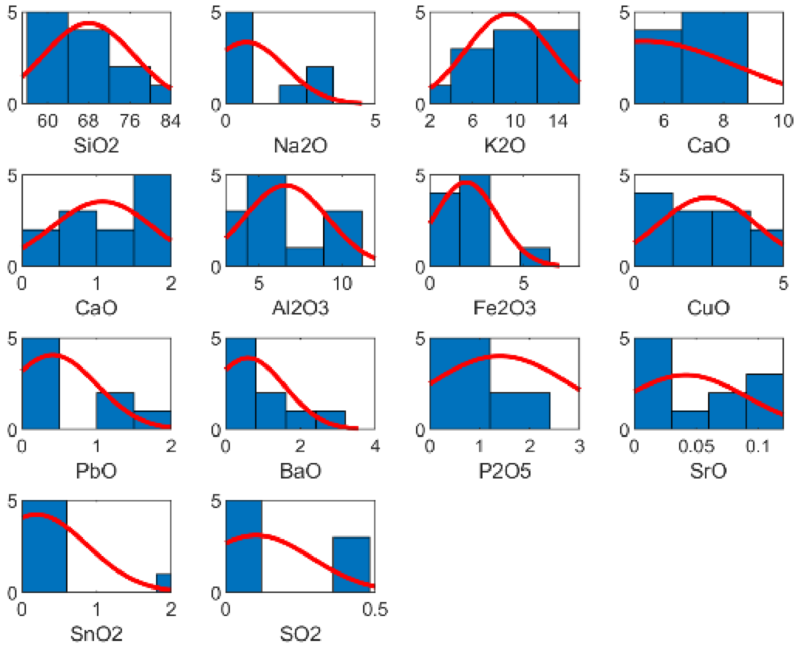

Figure 5. Normal fitting frequency distribution histogram of high potassium glass

According to Bootstrap method, it is predicted that the chemical composition content of high potassium glass before weathering can be expressed as follows: silicon dioxide content 67.9842 ± 2.4888%; Sodium oxide content 1.2869 ± 0.695%; The potassium oxide content is 9.3308 ± 3.9203% (see the table below for details). It is easy to know from the data in the table below that the initial content of chemical components in some original data is close to the range, or even not in the same order of magnitude with the range. For example, lead oxide, strontium oxide, etc., indicate that their chemical properties are unstable and are easily affected by the external environment.

Table 5. Prediction table of chemical composition of high potassium glass

Chemical composition	Forecast interval (%)	Chemical composition	Forecast interval (%)
SiO_2	67.9842±2.4888%	CuO	2.4525±1.6600
Na_2O	1.2869±0.6950	PbO	0.4117±0.5890
K_2O	9.3308±3.9203	BaO	0.5983±0.9821
CaO	5.3325±3.0925	P_2O_5	1.4025±1.4340
MgO	1.0792±0.6761	SrO	0.0417±0.4151
Al_2O_3	6.62±2.4915	SnO_2	0.1967±0.1965
Fe_2O_3	1.9317±1.6667	SO_2	0.1017±0.1850

Table 6. Prediction table of chemical composition of lead barium glass

Chemical composition	Forecast interval (%)	Chemical composition	Forecast interval (%)
SiO_2	53.4438±3.7678	CuO	23.5938±9.0944
Na_2O	0.7715±1.5383	PbO	10.4992±6.9498
K_2O	0.2585±0.3981	BaO	0.5983±0.9821
CaO	1.2315±1.4577	P_2O_5	0.9038±1.5706
MgO	0.4923±0.5455	SrO	0.2969±0.0829
Al_2O_3	3.1946±1.3852	SnO_2	0.0646±0.0410
Fe_2O_3	0.9331±1.4451	SO_2	0.0646±0.2750

3. Correlation analysis of chemical composition in different types of cultural relics

3.1. Model establishment

The chemical composition of cultural relic glass is mainly affected by the main raw materials, catalysts and environmental compounds; The use of principal component analysis is conducive to the analysis of the relationship between chemical components. Grey correlation analysis can quantitatively reflect the relationship of multiple factors.

3.2. Model solution

The glass types are classified into high potassium and lead barium by Excel.

Table 7. Analysis table of main components of high potassium glass

Feature vector	a_1	a_2	a_3	a_4	a_5	…
	-19.2692	-7.3249	-3.5877	-4.5822	-1.3939	
	-30.5724	-13.1557	-6.5492	-4.5155	-3.1977	
	…	…	…	…	…	
	-34.2254	-15.5754	-7.5326	-5.9519	-3.8970	
	-34.9951	-16.1222	-7.8615	-6.7066	-3.6205	
Characteristic value	0.2554	0.2106	0.1189	0.0775	0.0648	
Contribution rate	0.2554	0.4660	0.5849	0.6624	0.7272	
Cumulative contribution rate	0.4030	0.5906	0.7155	0.8320	0.9006	

Table 8. Lead barium glass principal component analysis table

Feature vector	a_1	a_2	a_3	a_4	a_5	…
	-3.9799	-9.2714	-17.3712	-0.1639	4.5238	
	14.3093	5.0634	5.9306	-1.8273	2.9653	
	…	…	…	…	…	
	7.25979	-2.7491	-10.3401	-2.0769	-14.2432	
	2.32049	-7.3198	-10.6806	-1.4442	-5.5724	
Characteristic value	3.5756	2.9487	1.6646	1.0847	0.9076	
Contribution rate	0.2554	0.2106	0.1189	0.0775	0.0648	
Cumulative contribution rate	0.2554	0.4660	0.5849	0.6624	0.7272	

It can be seen from the above table that the main components of lead barium glass are highly independent, that is, the correlation between their chemical components is weak.

3.3. Grey relational analysis

As shown in the Table 9 and Table 10, the order of influence degree of correlation between chemical components in lead barium glass is: Al_2O_3>BaO>PbO)>MgO>SrO>CaO)>K_2O>CuO)> Fe_2O_3> Na_2O> P_2O_5> SO_2>SnO_2.

As shown in the Table 9 and Table 10, the order of influence degree of correlation between chemical components in high potassium glass is: Al_2O_3>CuO>P_2O_5>MgO>K_2O>CaO>Fe_2O_3>PbO>SnO_2> SrO>BaO>SO_2>Na_2O.

Table 9. Correlation of chemical composition of different types of glass relics

Correlation index	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3
Hyperkalemia	0.8996	0.9200	0.9212	0.9315	0.9531	0.911
Lead barium	0.8495	0.9073	0.9031	0.9108	0.9318	0.8971

Table 10. (Continued) correlation of chemical composition of different types of glass relics

Correlation index	CuO	PbO	BaO	P_2O_5	SrO	SnO_2
Hyperkalemia	0.9151	0.9343	0.9357	0.8958	0.9242	0.8843
Lead barium	0.9308	0.8735	0.8546	0.9166	0.8637	0.8665

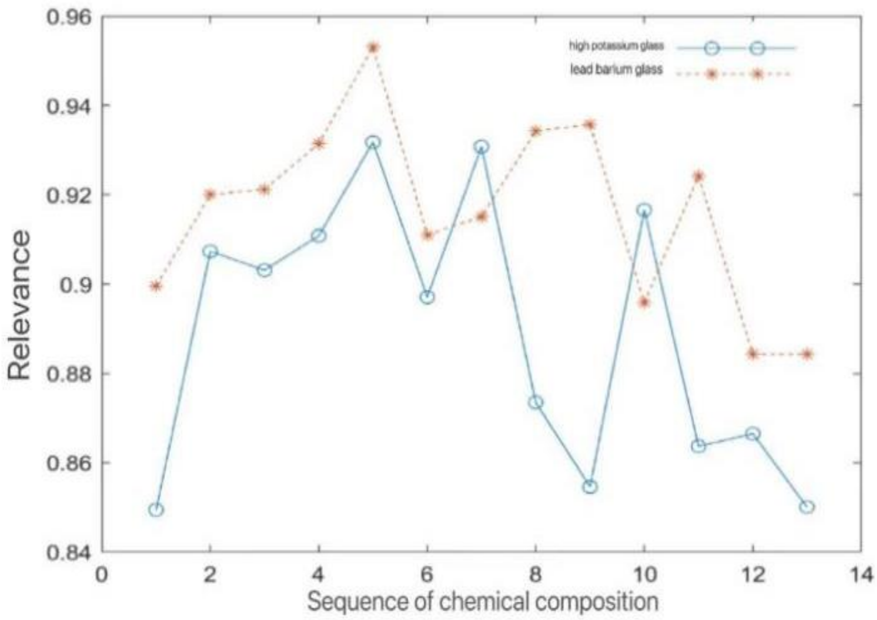

Figure 6. SiO_2 Correlation with other chemical components

The broken line diagram can directly show the difference in the direct correlation between the chemical composition of high potassium glass and lead barium glass. The main difference in the correlation degree between the chemical components of high potassium glass and lead barium vitrification and SiO_2 is significantly reflected in BaO and PbO. In lead barium glass, the correlation degree between the components of BaO and PbO and SiO_2 is weaker than that between the components of high potassium glass BaO and PbO and SiO_2, indicating that BaO and PbO are more independent in lead barium glass and have irreplaceable effects of other chemical components, which also confirms the reason why the main components of lead barium glass are not obvious.

4. Conclusions

This model focuses on data processing and statistics, which is presented in the form of tables and images, greatly improving the query efficiency; The paper gives a large number of figures, which are clear and clear in sections. Although it is intuitive and easy to understand, the reasoning is rigorous, simple and in-depth, and the results are accurate. The model has strong operability and is easy to popularize and apply; The model makes full use of the information given by the topic, uses programming algorithms and checks them to ensure the scientificity and preciseness of the problem-solving method; Preprocess the data to make the data more perfect and ensure the accuracy of the model.

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