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A NEW SCHEME OF THE ENVIRONMENTAL CLASSIFICATION STANDARDS FOR THE BRONZE CULTURAL RELIC'S PRESERVATION IN MUSEUMS

The environmental risk classification of the metal relics is usually determined by the corrosion rate of the metal but it is difficult to monitor the deterioration of the metal relics directly. A strong relationship exists between indoor exposure, the air quality classification of atmospheric corrosion, and the actual deterioration of metal relics. The copper-silver hanging plate method requires a long period of environmental exposure and has certain hysteresis, thus reflecting the current environmental quality of the museum in real time poses some difficulties. However, the application of the environmental reactivity monitor (ERMs) based on the piezoelectric effect can solve the above problems. The invented quartz crystal microbalance (QCM) reactivity monitoring device is applied to study the influence of temperature and humidity on the corrosion of the bronze-simulated materials and the relationship between the corrosion depth rate of the bronze-simulated materials and the frequency change of the crystal oscillator. Then, the recommended classification range of temperature and humidity and the air-quality classification standards for the preservation environment of the bronze cultural relics in museums are proposed.

1. INTRODUCTION

Museums are repositories of cultural heritage and are responsible for preserving the collections for the benefit of the present and future generations. The key to the stewardship role is the management of indoor conditions to prevent the deterioration of vulnerable objects. Preventive control measures are required to keep the indoor microclimate within

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the conservation limits by controlling the environmental conditions within certain parameters.

In the preservation environments, several environmental factors can cause the degradation of the culture relics including temperature, humidity, particulates, and gaseous pollutants. The main disease of the metal relics is the corrosion and the corrosion process is mostly the electrochemical corrosion [1]. Because the temperature and humidity change and the deposition of the gaseous pollutants provide the passage for the corrosion, the water film is formed on the metal surface. The relative humidity of the environment is the key factor that affects the formation of water film on the metal surface and the temperature affects the speed of the reaction process, both of which affect the corrosion rate of the metal [2, 3]. At the same time, the temperature change will cause a corresponding change in the relative humidity. Therefore, this study will consider the effect of the temperature and humidity at the same time, and the temperature and humidity will be considered as the first level of the environmental risk assessment.

The corrosion rate of copper is used as a standard for the environmental quality classification sometimes but the direct monitoring of the metal relic's deterioration is difficult to achieve. Therefore, Purafil developed the copper-silver hanging plate method, which can be adopted not only to detect the concentration of pollutants in the environment but also to distinguish the different types of pollutants. It was applied in many museums to monitor the ambient air quality. However, the copper-silver hanging plate method requires a long period of environmental exposure with a certain hysteresis [4, 5]; it is difficult to reflect the museum's current environmental quality status in real-time.

Air monitoring can provide the required short-term data in real-time for the pollution control program in the museum but it requires stringent requirements on the monitoring instrumentation and methodologies. However, the application of the Environmental reactivity monitors (ERMs) based on the piezoelectric effect can solve this problem effectively which can be combined with the computer and other auxiliary equipment to realize the real-time response to the frequency change of the crystal wafer. Therefore, the measured air quality status of the environment can be reflected in a relatively short time [6]. The reactivity monitoring has been taken a step further through the development of a real-time monitoring device employing metal-plated quartz crystal microbalances (QCMs). These microprocessor-controlled devices can measure the total environmental corrosion attributable to gaseous pollutants. ERMs employing QCMs can detect and record changes <1 ppb. This ability allows for the precise monitoring of changes in the microenvironment in the museum.

In this study, the corrosion depth rate of the simulated bronze cultural relic's material and the change of the crystal oscillator plate with temperature and humidity are monitored by the reactivity of the quartz crystal microbalance (QCM), and the acceptable temperature and humidity range for the bronze cultural relic's preservation is determined at first. Then, the recommended classification range of the temperature and humidity and the air-quality classification standard for the preservation environment of the bronze cultural relics in museums are proposed. Finally, the simulated modeling and the corrosion prediction of the bronze cultural relics are carried out and the real-time monitoring data in eight showcases are verified.

2. MATERIALS AND METHODS

Environmental reactivity monitoring device. The reactivity monitoring is a real-time monitoring device employing metal quartz crystal microbalances (Fig. 1). The environmental reactivity monitors employing QCMs can provide real-time information on the amount of corrosion occurring due to the presence of gaseous pollutants. This device monitors corrosion continuously, which allows for preventive action to be taken before serious damage has occurred. Appropriate reactivity and alarm levels for a particular application can be easily adjusted.

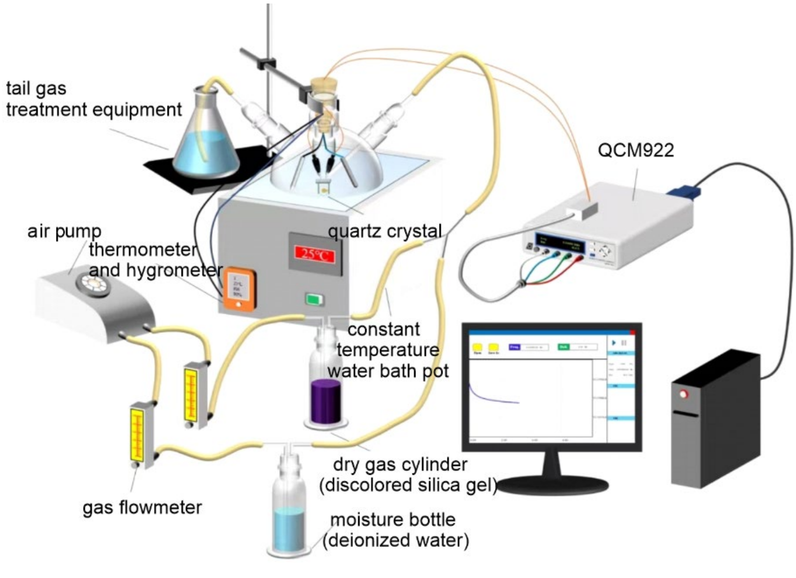

Fig. 1. The environmental reactivity monitoring device

This device may be operated independently as a battery-operated unit, and the monitoring data can be uploaded to a PC for viewing or graphing. It may also be wired directly into a central computer system. By making use of the unit's ability to interface with computer systems, up-to-the-minute information on the levels of corrosive contaminants can be obtained. Environmental classification databases can be established and maintained to provide historical data.

Basis. QCMs can reflect the variable relationship between the gaseous pollutants and the metal corrosion effectively. Chris [7] proposes a standard classification scheme that relates the corrosion rates to the environmental classification directly. The classification results of the air quality in the silver and copper preservation environment for the museum environment proposed by Purafil USA are indicated. If an environment behaves according to C1 standard (i.e., corrosion depth rate is less than 9 nm within a range of 30 days), it is considered that there is no other way to improve the environment economically. If the general reactive monitoring acceptance criteria for C2 (if an environment behaves according to C2 standard, i.e., corrosion depth rate is less than 15 nm within a range of 30 days) are satisfied, it is generally accepted that it is a sufficiently controlled environment to prevent the decay or deterioration of objects and culture relics [8, 9].

Until now, a typical application of reactive monitoring is the characterization of the outdoor air for ventilation, the identification of "hot spots" within the facility, and the effectiveness of various preventive measures. Besides, reactive monitoring can be applied to study the causal relationship between the gaseous pollutants of the preservation environments and the possible damage to the artwork and the historical culture relics.

Our research team has been working on the corrosion of the metal cultural relics for many years and studied the corrosion behavior of the metal materials exposed to pollutants in the single and compound environment by the quartz crystal microbalance (QCM) reactivity monitoring method [10, 17]. This paper studied the risk assessment of the environment for the bronze cultural relic's preservation in the museum and proposed the environmental classification standards for the bronze cultural relic's preservation in the museum.

3. RESULTS AND DISCUSSION

3.1. THE INFLUENCE OF TEMPERATURE AND HUMIDITY ON BRONZE CORROSION

The atmospheric corrosion of the metal cultural relics essentially is an electrochemical corrosion process, so it can be seen that the formation of water film on the surface of the metal cultural relics is the necessary condition for corrosion to occur. The temperature and humidity are important factors affecting the preservation environment of cultural relics in the museum, which is also the basic indicator [11] and plays a major role in the formation of water film on the metal cultural relic's surface.

The temperature of the environment affects the chemical reaction rate of the metal surface and the solubility of the soluble pollutants, the humidity affects the formation, the condensation thickness, and the existence time of the liquid film on the metal material surface. The corrosion of the bronze cultural relics is mostly affected by the temperature and humidity [9–16]. In general, the effect of the temperature on the metal atmospheric corrosion is small and difficult to predict. On the one hand, the increase of the temperature will reduce the formation rate of water film on the metal surface, thereby slowing down the occurrence of corrosion. On the other, high temperature will promote the condensation of water film on the metal surface and accelerate the chemical reactivity, thereby aggravating the corrosion of the metal cultural relics.

To better classify the corrosion level of the simulated bronze cultural relics materials under different temperatures and humidity, the average corrosion depth of metal per unit time is adopted to calculate the corrosion rate of the metal. The calculated dew point temperature, the corrosion rate, and the frequency change values of the crystal oscillator under different temperature and humidity conditions are shown in Table 1. The surface weight of the copper-plated crystal oscillator increases with the increase of the ambient temperature under the same relative humidity, indicating that the reactivity acceleration effect of the temperature during the metal corrosion process is greater than its inhibitory effect on the metal surface water film formation process.

Table 1

The dew point, corrosion depth rate, and frequency change ($|\Delta f|$) of the crystal oscillator at various temperatures (T) and relative humidities (RH)

T [°C]	RH [%]	Dew point [°C]	Corrosion depth rate [nm]		$\|\Delta f\|$ [Hz]	
			24 h	30 d	24 h	30 d
10	20	–12.1	0.129	3.092	33.6	645.2
	30	–10.3	0.237	5.498	43.2	838.1
	40	–2.5	0.307	7.153	55.3	1067.2
	50	0.4	0.412	9.171	75.8	1502.4
	60	5.5	0.442	9.741	77.4	1696.0
	70	7.6	1.02	10.649	183.5	1773.4
	80	10.4	1.138	11.867	169.5	1816.1
	90	11.7	1.436	15.078	224.3	2178.2
	100	12.3	1.984	20.032	304.1	2563.8
20	20	–5.1	0.165	3.795	39.6	752.4
	30	0.2	0.274	6.302	50.3	960.7
	40	5.5	0.454	10.442	76.4	1597.7
	50	10.4	0.481	10.582	81	1682.3
	60	12.6	0.632	14.583	89.7	2038.1
	70	15.3	1.05	15.091	132.7	2175.2
	80	19.5	1.252	15.638	189.1	2269.4
	90	20.2	1.534	15.872	238.9	2317.6
	100	22.1	2.227	21.152	362.3	2954.8
30	20	4.3	0.205	4.715	46	855.0
	30	8.5	0.206	4.738	59.3	1186.2
	40	13.3	0.375	8.625	69.9	1328.1
	50	15.2	0.602	13.846	105.1	2019.3
	60	17.3	0.885	12.390	135	1937.2
	70	23.6	1.108	15.512	207	2193.0

Table 1

The dew point, corrosion depth rate, and frequency change (|Δ*f*|)
of the crystal oscillator at various temperatures (*T*) and relative humidities (*RH*)

T [°C]	*RH* [%]	Dew point [°C]	Corrosion depth rate [nm]		|Δ*f*| [Hz]	
			24 h	30 d	24 h	30 d
	80	27.2	2.021	19.637	307.1	2568.5
	90	28.4	2.337	21.966	358.1	2960.9
	100	30.5	3.042	27.832	461.2	3638.4
40	20	11.3	0.279	6.417	58.4	1121.2
	30	15.2	0.352	8.096	70.3	1356.7
	40	21.3	0.573	13.179	107.3	1932.4
	50	25.1	0.825	11.552	128.7	1793.2
	60	28.6	1.032	14.650	220.3	2052.3
	70	31.4	1.438	15.771	238.8	2317.7
	80	33.2	2.014	19.564	379.6	2546.8
	90	34.9	2.683	25.432	421.9	3287.3
	100	35.1	3.469	30.875	606.3	4032.9
50	20	20	0.354	7.788	70.5	1339.5
	30	24.8	0.381	8.382	73.8	1402.2
	40	30.3	0.625	13.75	115.9	2002.3
	50	34.7	1.031	14.642	230.4	2051.5
	60	36.3	1.146	15.752	246.5	2313.2
	70	43.5	1.472	16.483	306.4	2389.2
	80	46.6	2.687	25.439	467.9	3287.7
	90	49.4	3.029	26.952	518.4	3615.3
	100	50.2	4.183	36.392	623.9	5672.3
60	20	26.8	0.497	10.843	98.9	1928..5
	30	32.4	0.633	14.688	124.6	2082.5
	40	37.9	0.935	14.069	172.3	2791.2
	50	42.3	1.372	15.307	263.4	2273.2
	60	45.8	1.728	16.760	310.2	2439.0
	70	52.3	1.873	21.165	375.2	2865.3
	80	55.4	3.269	29.094	537.5	3093.4
	90	59.2	3.546	31.559	623.8	4121.4
	100	60.2	4.529	39.401	713.7	6588.3

In addition, metal corrosion is mostly an electrochemical process. Theoretically, when the relative humidity of the environment is 10%, the water film on the metal surface is difficult to form and the electrochemical corrosion channel has not been established, so the electrochemical corrosion of the metal will not happen. However, the experimental results show that the surface weight of the copper-tin alloy crystal oscillator changes after being exposed to the environment with a relative humidity of 10% at a certain temperature for 24 hours. It shows that the metal copper surface corrosion still occurs in the low relative humidity environment, which is chemical corrosion with a relatively slow reaction. It also shows that the atmospheric corrosion process of the metals is more complex and the use of the comprehensive indicators is conducive to the risk assessment of the cultural relic's preservation environment.

3.2. THE PRELIMINARY CLASSIFICATION OF THE PRESERVATION ENVIRONMENTAL RISK FOR THE BRONZE CULTURAL RELICS BASED ON TEMPERATURE AND HUMIDITY

The frequency changes and the corrosion depth rates of the copper-tin alloy crystal oscillator of the simulated bronze material exposed to different relative humidity environments for 24 h fitted at different temperatures are shown in Fig. 2. The curve conforms to the S-type fitting, which is consistent with the study results of the effect of relative humidity on copper corrosion by Samie et al. [17]. Measuring the frequency change of the crystal oscillator with QCM can reflect the corrosion degree of the metal surface very well.

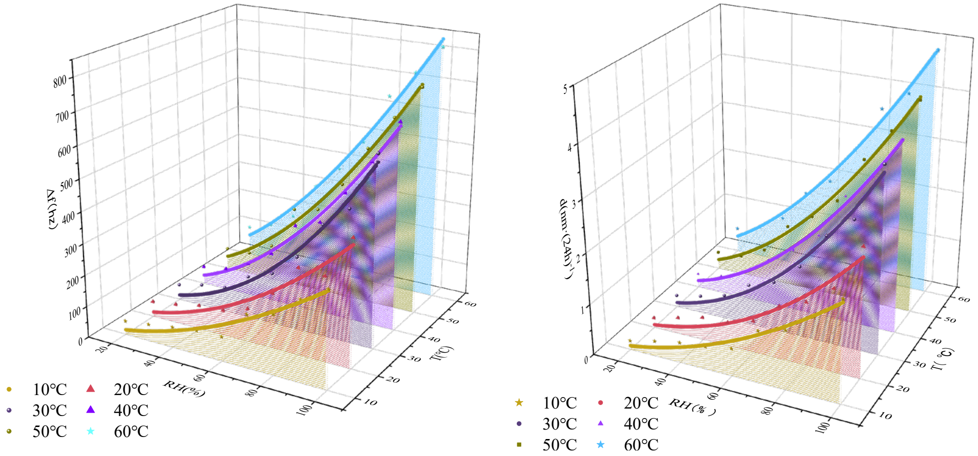

Fig. 2. The frequency changes ($|\Delta f|$) and corrosion depth rates (d) of the copper-tin alloy crystal oscillator of the simulating bronze material exposed to the different relative humidity (RH) environments for 24 h fitted at different temperatures (T): frequency variation chart (left), corrosion variation chart (right)

It is evident from the trend of the fitting curve that the frequency change amplitude will jump when the relative humidity is greater than 60% at a certain temperature, which is consistent with the relationship between the relative humidity and the number of water molecule layers on the metal surface. The metal surface can absorb about 15 layers of monomolecular water in the environment with a relative humidity ≥60%, which already shows characteristics close to that of free water [18, 19].

When the dew point decreases below the freezing point, the water vapor precipitated from the air will not condense into liquid water but solidify into solid water directly.

The tiny microscopic ice particles will adhere to the surface of the object to form frost. The dew point at this time is defined as the dew point temperature. The dew point is related to the relative humidity, the higher the relative humidity, the closer the dew point to the air temperature is. When the relative humidity reaches 100%, the dew point and air temperature will decrease, and vice versa. When the temperature is determined, the water vapor content in the air can be known by the dew point, so the dew point is an indicator of the absolute temperature [20, 21].

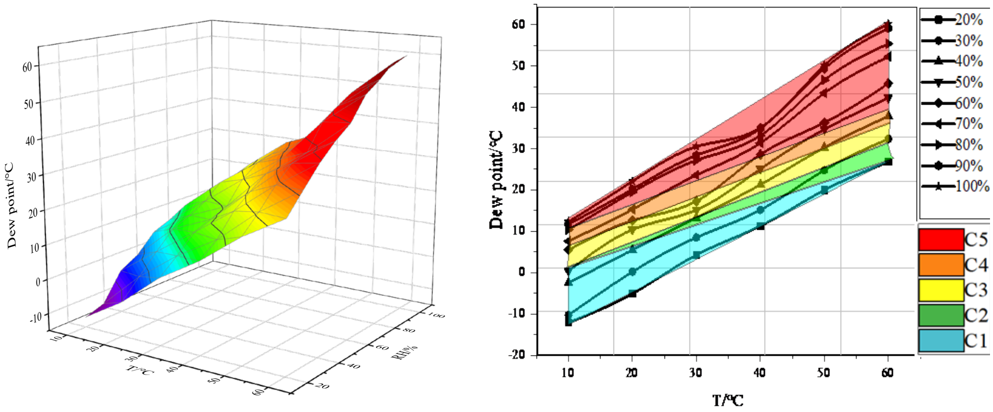

Fig. 3. The relationship between the temperature, humidity and the dew point and a condensation risk rating chart (left), temperature, humidity, and dew point, condensation risk rating chart (right)

The relationship between the temperature and humidity and the dew point is shown in Fig. 3. The formation of water film (the condensation behavior) is related to the temperature and humidity of the environment (Fig. 3, left). The statistical results show that the thickness of the water film condensed on the metal surface has a very important influence on the corrosion of the metal. When the humidity is lower, the corrosion degree of the metal surface is lighter because the water film is thinner and less pollutants are dissolved. With the increase of the relative humidity, the water film on the metal surface will become thicker and the pollutants dissolved in the water film from the air will increase, causing more serious metal corrosion. The temperature and humidity levels shown in Fig. 3 right are classified according to the condensation difficulty, which is the atmospheric liquid film corrosion difficulty of the metal cultural relics. The first and second levels are relatively safe and in the low-risk temperature and humidity range. Referring to the classification standard of the air cleanliness and pollution degree by Purafil USA, and taking the C1 standard of the copper corrosion depth rate (<9 nm/30 days) as a reference [22], the preliminary classification of the preservation environmental risk for the bronze cultural relics based on temperature and humidity is proposed shown in Table 2. From the table, the classification of the preservation environmental risk includes four risk levels: C1 – acceptable, C2 – low risk, C3 – medium risk, C4 – high risk.

Table 2

The preliminary classification of the preservation of environmental risk for the bronze cultural relics based on temperature and humidity

Class	Risk level	$\|\Delta f\|$ [Hz]		Corrosion depth rate [nm]	
		24 h	30 d	24 h	30 d
C1	acceptable	<62±5	<1488±5	<0.37	<9
C2	low	<91±5	<2175±5	<0.7	<15
C3	medium	<130±5	<3250±5	<0.95	<25
C4	high	>135	>3255	>0.95	>25

Considering the error deviation in the quartz crystal oscillator, the variation range is set to 5 Hz.

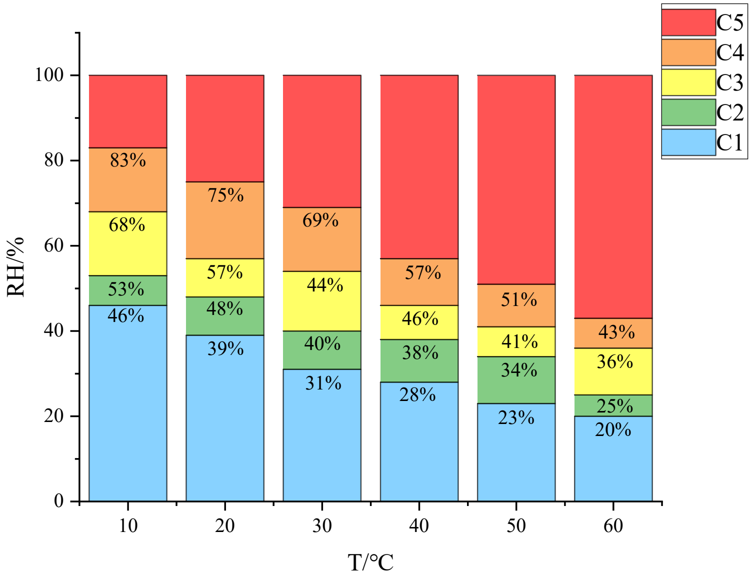

Fig. 4. The recommended classification range of temperature (*T*) and humidity (*RH*) for the preservation of the bronze relics in museums

Based on Table 2 and Fig. 3, the recommended classification range of the temperature and humidity for the preservation of the bronze relics is own in Fig. 4. It is recommended that the environmental temperature and humidity should be controlled within the range of C2 most of the time. The temperature and humidity should be adjusted according to the actual air quality in the museum.

3.3. THE AIR-QUALITY CLASSIFICATION STANDARD FOR THE PRESERVATION ENVIRONMENT OF THE BRONZE CULTURAL RELICS I

To improve the environmental risk classification standards of the museum, our research team also studied the corrosion trend of the simulated bronze materials under the action of single or compound pollutants. According to the reports [23–25], the temperature of the museums at home and abroad is mostly controlled at 15–25 °C and the relative humidity is mostly controlled at 40–60% to study the influence of the pollutants on the corrosion of the bronze cultural relics simulated materials.

Based on the frequency and the corrosion rate changes of the simulated bronze material copper-tin alloy crystal oscillator under different concentrations of pollutant gases at 20 °C and the relative humidity of 50%, the corrosion rate of the simulated bronze cultural relics material and the frequency of the crystal oscillator are fitted (Fig. 5). From the fitting data, it can be seen that the R^2 value after fitting is higher than 0.90, indicating that the fitting degree of the curve is high.

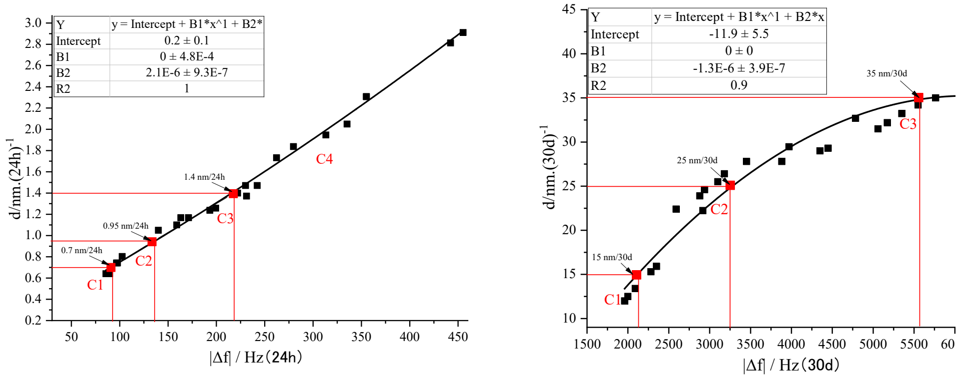

Fig. 5. The fitting diagram of the corrosion depth rate (*d*) and the variation of the crystal vibration piece (|Δ*f*|) of the bronze relic simulation material: 24 h (left), and 30 d (right) fitting diagrams

Table 3

The air quality classification standard for the preservation environment of the bronze cultural relics in museums

Class	Risk level	|Δf |/Hz		Corrosion depth rate/nm	
		24 h	30 d	24 h	30 d
C1	acceptable	<91±5	<2175±5	<0.70	<15
C2	low	<130±5	<3250±5	<0.95	<25
C3	medium	<222±5	<5665±5	<1.4	<35
C4	high	>227	>5670	>1.4	>35

Considering the certain error deviation in the quartz crystal oscillator, the variation range is set to 5 Hz.

Based on the relationship between the change of the reactive monitoring crystal oscillator and the corrosion depth rate under the contamination conditions, referring to the air quality classification results by Purafil (USA) and taking the C2 standard of copper corrosion rate (<15 nm/30 d) as a reference, the air-quality classification standard for the preservation environment of the bronze cultural relics in museums is proposed (Table 3). The air-quality classification standard includes four risk levels: C1 – acceptable, C2 – low, C3 – medium, C4 – high. If the air-quality risk level meets the C2 standard, it is considered a well-controlled environment that can prevent corrosion effectively.

3.4. CASE STUDY

The air-quality classification standard for the preservation environment of the bronze cultural relics in museums was trialed in eight showcases in the Shanghai Museum. The purpose was to examine the feasibility of the air quality classification standard and identify the necessity for any immediate modifications.

The environmental temperature and humidity of eight showcases were controlled at 20±2 °C and the relative humidity of 50±5%, which is at the range of C2 according to the recommended classification range of the temperature and humidity for the preservation of the bronze relics in museums.

All the cultural relics in display cases 1–8 for the risk assessment are bronze wares. According to the specific situation of the exhibition, the risk levels of the cultural relics preservation environment are divided according to the real-time monitoring data in the museum showcases. The total monitoring time was 60 days, investigated variable – real-time monitoring.

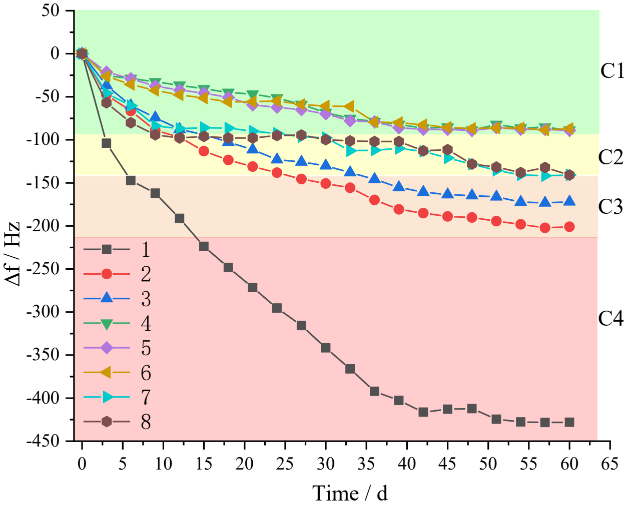

Fig. 6. 24 h average frequency change curve of the QCM reactivity monitoring in eight showcases

Figure 6 shows the 24 h average frequency change curve of the QCM reactivity monitoring for eight showcases, which indicates the average change trend of the environmental quality of eight showcases within 60 days. According to Table 3, the air quality classified level in the showcase Nos. 4–6 is C1; the air quality classified level of the showcases Nos. 7 and 8 is C1 in the first 30 days and C2 in the next 30 days; the air quality classified level in showcases Nos. 2, 3 is C1 from the 1st to 13th week, C2 from the 13th to 30th day, and C3 from the 30th to 60th day;

The situation of the showcase no.1 is relatively worse. The air quality changes rapidly in the first 15 days. Its air quality classified level is C4 from the 15th to the 60th day. The air quality data is at a high-risk level, which causes the corrosion of the bronze cultural relics and the occurrence of bronze disease.

In order to verify the air-quality classification standard for the preservation environment, the average corrosion depth rate was calculated and the risk level was classified for the bronze cultural relics in eight display cases as shown in Table 4.

Table 4

Corrosion rates at various risk levels

Display case	1–30 days	Corrosion class	31–60 days	Corrosion class
1	2.32 nm/24 h	C4	3.54 nm/24 h	C4
2	0.79 nm/24 h	C2	1.03 nm/24 h	C3
3	0.68 nm/24 h	C2	0.97 nm/24 h	C3
4	0.32 nm/24 h	C1	0.43 nm/24 h	C1
5	0.37 nm/24 h	C1	0.47 nm/24 h	C1
6	0.35 nm/24 h	C1	0.49 nm/24 h	C1
7	0.53 nm/24 h	C2	1.02 nm/24 h	C2
8	0.61 nm/24 h	C2	1.07 nm/24 h	C2

It is verified that the change of the QCM reactivity monitoring crystal oscillator can reflect the air quality level of the bronze cultural relics preserved in the museum. Therefore, the QCM online monitoring documented the feasibility of the air-quality classification standard for the preservation environment of the bronze cultural relics in museums.

4. CONCLUSIONS

The reactivity monitoring environmental analysis method has been applied in many museums currently. The effectiveness of the air monitoring technique is that many pollutants of the major concern in preservation environments are corrosive and thus can be monitored by reactive monitoring easily.

Air monitoring is central to any environmental control program for achieving and maintaining air-quality standards, based on the presence (or absence) of gaseous air pollutants. Such monitoring can also provide the short-term data required to manage and mitigate contaminant-specific episodes. In addition to direct application to contamination control programs, air-monitoring data may be employed for (1) the evaluation of long-term air-quality trends in a facility, and (2) research studies designed to determine relationships between pollutant levels and possible damaging effects.

Although this methodology primarily focuses on the special requirement of metal culture relics in museums, it can easily be extended to other environments and applicable objects, maintaining its basic structure due to different cultural relics and preservation environment should establish air-quality classification standards for the preventive protection of relics. On this basis, the method can serve to assess the health status of different cultural relics from a scientific and practical point of view.

Our research team has been cooperating with several museums and institutions to develop and refine techniques so that the conservators can accurately evaluate the destructive potential of their environments to the cultural relics and materials entrusted to their care.

In this study, a new scheme of the environmental classification standards for bronze cultural relics preservation in museums has been promoted by our research team. The quartz crystal microbalance (QCM) reactivity monitoring method was applied to the bronze culture relics in museums. The recommended classification range of the temperature and humidity for the preservation environment was based on the investigation of the bronze relic's simulation materials. Furthermore, the air-quality classification standard for the preservation environment is proposed according to the corrosion depth rate of bronze simulation materials and crystal vibration.

The analysis shows that the temperature and humidity for the preservation of the bronze relics in museums should be controlled at 20±2 °C and 50±5%, respectively. The general reactivity monitoring acceptance standard of C2 is accepted to sufficiently control the deterioration of culture relics. According to the air-quality classification standard for the preservation environment of the bronze cultural relics in museums, the C2 standard conditions are: $|\Delta f|$ max 130 Hz/24 h, 3250 Hz/30 d with allowing ±5 °C change during the 24 h, maximum corrosion depth rate 0.95 nm/24 h, 25 nm/30 d.

This new scheme of the environmental classification standards can provide a rich guide with all the needed information in terms of the museum's indoor environment parameters for the museum officials to implement strategies and enhance the current conditions of the museums.

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