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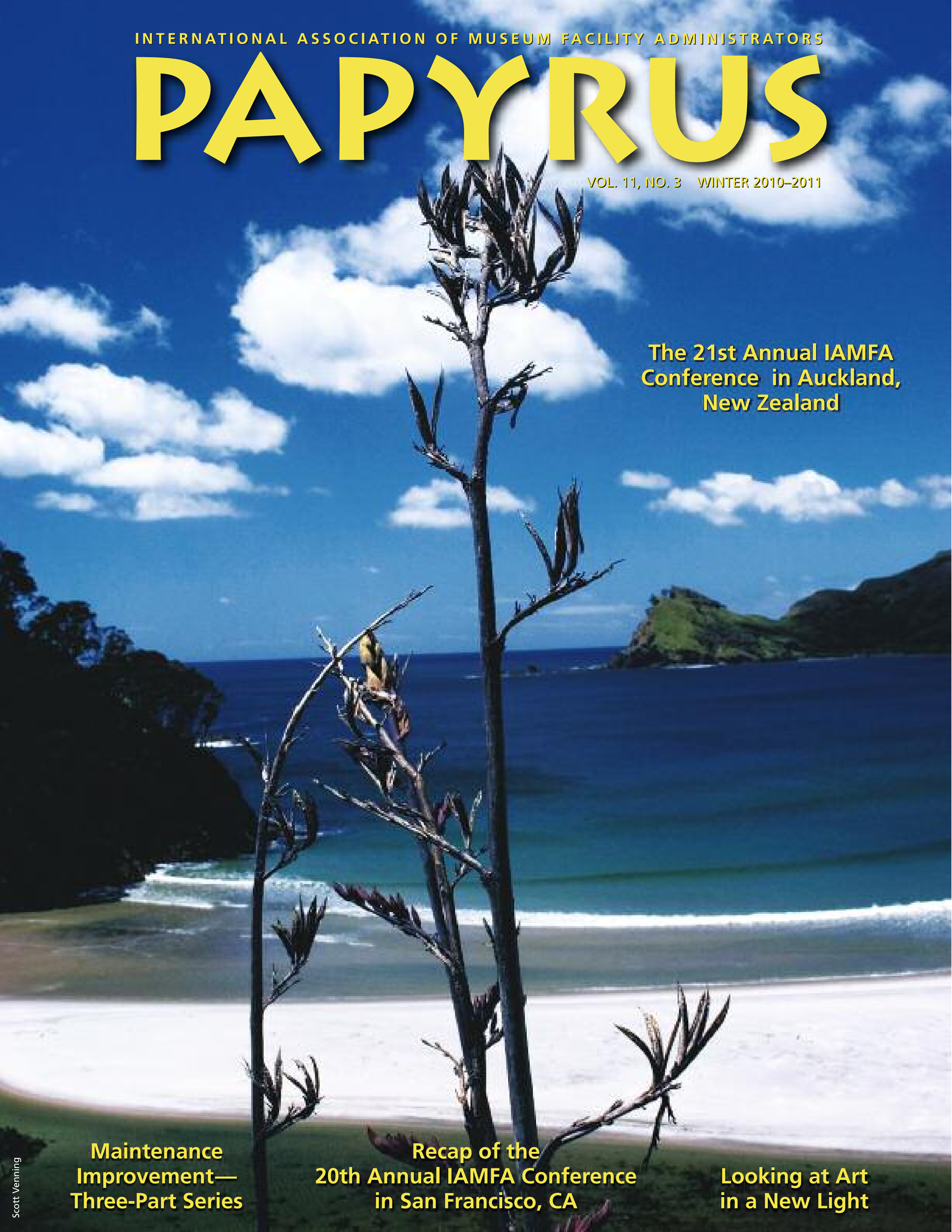

Scott Venning

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Looking at Art in a New Light

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Cover photo: *Tall woody stems with deep red flowers rise from the heart of flax plants, heralding the beginning of summer. Photo: Scott Venning*

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Air-Quality Standards for Preservation Environments

Considerations for Monitoring and Classification of Gaseous Pollutants

By Chris Muller

Introduction

In preservation environments, there are a number of environmental factors which can cause the degradation of materials and artifacts. Among these are temperature, humidity, particulates, and gaseous pollutants. Of these, gaseous pollutants are the most destructive.

Gaseous pollution today is caused primarily by the burning of fuels in power plants, factories, commercial and domestic buildings, and automobiles. The two main types of gaseous urban air pollutants can be classified either as acidic or oxidizing. Over the years, these two types have merged, and now the three main pollutant gases found throughout the industrialized world are sulfur dioxide (SO_2), ozone (O_3), and nitrogen dioxide (NO_2). Others of primary concern include chlorides (chlorine [Cl_2] and hydrogen chloride [HCl]), acetic acid (CH_3COOH), and formaldehyde (HCHO).

While automotive and/or industrial emissions are considered the largest contributors of SO_2, O_3, NO_2, and chlorides, there are also many significant sources of internally-generated pollutants. Materials and activities associated with restoration and conservation laboratories, many artifacts and archival materials, and employees and patrons themselves, can contribute to the overall pollutant load in preservation environments.

Although gaseous pollutants are a major worldwide environmental concern, sources of gaseous pollutants, their introduction and migration through museums, and their interactions with artifacts, are the least studied and least understood area of concern within preservation environments. General reviews of pollutant sources and object vulnerabilities and information and guidelines for gaseous pollutants were scarce until the 1990s.

There is some information, research, and consideration of common urban pollutants and their effects on artwork and archival materials, as well as guidelines for their control. Generally, these guidelines call for interior concentrations of gaseous pollutants to be maintained as low as attainable by gas-phase air filtration. The most commonly cited control levels for gaseous pollutants are shown below.

Sulfur dioxide	<0.35 - <1.0 ppb
Ozone	<0.94 - <12.5 ppb
Nitrogen dioxide	<2.65 ppb
Chlorine	<1 - 3 ppb
Hydrogen chloride	<1 - 3 ppb
Acetic acid	<4 ppb
Formaldehyde	<4 ppb

Air-Monitoring Tools and Techniques

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, if any, between pollutant levels and possible damaging effects. Air-quality measurements in preservation environments often make stringent demands on monitoring instrumentation and methodologies. Special modifications and protocols are often needed to adapt the techniques for use in these environments.

Several characteristics of any measurement technique must be evaluated to determine its appropriateness for use in (indoor) air-quality monitoring. Among the more important characteristics are sensitivity, cost, and complexity. Sensitivity is a particularly demanding parameter for indoor environments where near-ambient levels of many pollutants may be encountered, and control levels are approaching the sub-parts per billion (ppb) level. Likewise, cost may be quite important when deciding on a measurement technique, particularly in large surveys. A final point of consideration is the complexity of the technique, and the degree of skill and training required to obtain quality results. Other factors deserving consideration are selectivity and portability. Most measurement techniques are not optimized for all of these parameters, and one must weigh the various characteristics in order to best meet the desired goals. Often trade-offs will be necessary in selecting the techniques to be used for a specific study.

Direct Gas Monitoring

The biggest problem today is not whether specified levels of air quality can be reached, but whether they can be accurately measured to ensure compliance with any standards or control criteria. One consideration faced in designing an (indoor) air-quality monitoring program is the choice of passive vs. active sampling. The (relatively) immediate feedback of an active monitor is a most desirable aspect, and is what often precludes the use of passive monitors. Another consideration is the option of direct versus indirect monitoring techniques.

Electronic devices designed for real-time gas monitoring respond to changes in the measured variable very quickly. They are capable of detecting pollutant levels in the ppb range, and are available for a wide range of pollutants. Individually, chemical pollutants may be monitored using various analytical techniques to provide both the sensitivities and selectivities required to perform accurate low-level real-time monitoring. The major disadvantage to the use of real-time gas monitors is the relatively high cost when compared to other techniques. Table 1 lists a number of different pollutants and the levels which can be monitored with real-time monitors.

Reactivity Monitoring

Even though it is possible to identify and quantify (almost) all chemical species one may encounter in preservation environments, the question still remains: "what do I do with this information?" To date, there has been no study performed (or at least published) which provides definitive information as to the cause-and-effect relationship between specific levels of gaseous pollutants and the damage they may cause to paper documents, artwork, and historical artifacts. Because of this, a number of institutions are turning to environmental classification via what is referred to as reactivity, or corrosion, monitoring. The validity for this air-monitoring technique lies in the fact that many of the pollutants targeted for control are corrosive in nature and, therefore, can be effectively measured using this technique.

Reactivity monitoring can characterize the destructive potential of an environment. The growth of various corrosion films on specially prepared copper, silver, and/or gold(-plated) sensors provides an excellent indication of the type(s) and level(s) of essentially all corrosive chemical species present in the local environment. Both passive and real-time reactivity monitors are currently available, and each can be used to gather important information on gaseous pollutants and their levels in the environment.

Environmental Reactivity Coupons (ERCs)

ERCs (Figure 1) are passive monitors typically exposed to the environment for a period of 30 to 90 days, then analyzed for the amount and type of corrosion which has formed. This technique can provide cumulative reactivity rates, an assessment of "average" environmental conditions over time, and an indication of the type(s) and relative level(s) of corrosive gaseous pollutants.

ERCs may be used to indicate the presence of SO_2, O_3, NO_2, Cl_2, and many other corrosive materials which can cause deterioration of metals, cellulose, and organic materials. ERCs originally used only copper reactivity to establish environmental classifications. However, copper is not sufficiently sensitive to many of those pollutants ubiquitous to most urban environments—the same environments in which most museums, etc. are located. Further, copper coupons cannot detect the presence of chlorine, a particularly dangerous contaminant to metals.

With this in mind, the use of silver reactivity monitoring was developed for these unique environments. Silver is

Figure 1: Copper/silver ERC.

Table 1: Currently available real-time chemical/gas monitors

Pollutant	Concentration Range, ppb	Lower Detection Limit, ppb	Response time, sec	Selectivity	Susceptibility to Interferences
Ammonia	0-200	1.0	900	Medium	Low
Formaldehyde	0-1000	0.2	300	High	Low
Hydrochloric acid	0-200	1.0	900	Medium	High
Hydrogen sulfide	0-200	1.0	120	Medium	Low
Nitrogen oxides	0-200	0.1	90	NO-High, NO_2-Low	Low
Ozone	0-1500	1.0	50	High	Low
Sulfur dioxide	0-200	0.1	120	High	Low

sensitive to chlorine and, when used with copper reactivity monitoring, can be used to detect changes in the levels of gaseous pollutants in the ambient environment as small as 1 ppb, while also differentiating between different types of contaminants.

The corrosion reported from reactivity monitoring with ERCs is actually the sum of individual corrosion films. For copper coupons, sulfide and oxide films are most commonly produced and are reported as copper sulfide (Cu_2S) and copper oxide (Cu_2O), respectively. For silver coupons, sulfide, chloride, and oxide films may be produced and are reported as silver sulfide (Ag_2S), silver chloride ($AgCl$), and silver oxide (Ag_2O), respectively. Each coupon is analyzed as to the type and amount of film present and its relative contribution to the total corrosion produced.[1,2]

Environmental Reactivity Monitors (ERMs)

One consideration faced in designing an air-quality monitoring program is the choice of passive vs. active sampling. The immediate feedback of an active monitor is a most desirable aspect, and is what often precludes the use of passive monitors. The main limitation in the use of CCCs is their inability to provide a continuous environmental classification. To address this, reactivity monitoring has been taken a step further through the development of a real-time monitoring device employing metal-plated quartz crystal microbalances (QCMs, Figure 2).[3,4] These microprocessor-controlled devices are able to measure the total environmental corrosion attributable to gaseous pollutants. ERMs employing QCMs can detect and record changes <1 ppb. This ability is regarded as one of the main requirements for any real-time monitoring protocol to be used in preservation environments.

To date, there is only one commercially available ERM employing copper and silver-plated QCMs able to provide real-time information on the amount of corrosion occurring due to the presence of gaseous pollutants (Figure 3). This device monitors corrosion on a continuous basis, 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.

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.

Figure 2: Quartz crystal microbalance.

Figure 3: Environmental Reactivity Monitor.

Control Specifications

There has been little research done to determine what levels actually cause deterioration of historical artifacts and archival materials. Experience has come from determination of the normal background levels of the pollutants to which these materials have been exposed over the years. Some postulate that more deterioration has occurred in the past fifty years than in the previous two thousand. As stated at the beginning of this section, it was not until the Industrial Revolution, and more distinctly, "the Age of the Car" that global pollutant levels dramatically increased. "Normal" background pollutant levels measured in non-industrial versus industrial areas today frequently show differences of two orders of magnitude. This is illustrated in Table 2.

Table 2: Common levels of gaseous pollutants

Pollutant	Normal Background Concentrations	Peak Concentrations (Urban Areas)
Sulfur dioxide	6-30 ppb	100-750 ppb
Ozone	0.4 ppb	20-40 ppb
Nitrogen dioxide	1.0-1.5 ppb	40-100 ppb
Chlorine	0.06-0.6 ppb	20-130 ppb
Hydrogen chloride	20-50 ppb	200-450 ppb
Acetic acid	4-10 ppb	20-100 ppb
Formaldehyde	3-15 ppb	10-40 ppb
Hydrogen sulfide	5-10 ppb	100-500 ppb

Just as there are wide variations between background and peak gas concentrations, there are also wide variations in just what are considered acceptable levels for these pollutants. Some institutions specify that sulfur dioxide, nitrogen dioxide, and ozone are to be removed completely. Other sources recommend levels from fractional parts-per-billion up to the low parts-per-million (Table 3). One might argue that, although there is still considerable variation in the recommended allowable pollutant levels, at least attempts have been made to set standard levels.

Based on joint research performed by Purafil, Inc., the Dutch Government,[5] the Swedish Corrosion Institute,[6] and the Comitato Termotechnical Italiano (C.T.I.),[7] reactivity monitoring using either copper or silver corrosion rates are now preferred over direct monitoring of gaseous pollutants. It has become the standard for air-quality monitoring in Dutch government archives, and is being considered as an EU standard. These specifications are also shown in Table 3.

This environmental analysis method is currently being used by Purafil and a number of institutions and international government agencies, and has been described in the literature.[8,9]

Table 3: Control specifications for preservation environments

Contaminant/ Parameter Measured	Concentration ppb	Concentration μg/m³	Reactivity Level, Å/30 days
Sulfur dioxide	≤0.35-1.0	≤1-2.85	—
Ozone	≤2.65	≤1.8-24.5	—
Nitrogen dioxide	≤0.94-12.5	≤5	—
Chlorine	≤1-3	≤3-9	—
Hydrogen chloride	≤1-3	≤1.5-4.5	—
Acetic acid	<4	<10	—
Formaldehyde	<4	<5	—
Silver Corrosion	—	—	<40[a]
Copper Corrosion	—	—	<90[b]

[a]*With no sulfur corrosion evident.*
[b]*With no chloride corrosion evident.*

The amount of corrosion forming over any given period is a primary indicator of how well-controlled an environment may be. Where gas-phase air filtration is employed to maintain the interior concentrations of gaseous pollutants as low as possible, corrosion rates <15–20 Å/30 days range can be routinely maintained. Subsequent gas monitoring has indicated pollutant levels to be at or below the limits of detection for the analytical techniques employed. This "no detectable pollutants" scenario is being used to set up environmental classification systems based on reactivity monitoring. It is felt that, if an environment exhibits corrosion rates less than or equal to those in Table 3, there is nothing else which can be done, economically, to improve the environment.

Environmental Classifications

Table 4 lists a standard classification scheme which directly correlates corrosion rates to environmental classifications. These are being refined based on the results of testing and the specific needs of this market. Typical uses of reactivity monitoring to date have been for the characterization of outdoor air used for ventilation, the identification of "hot spots" within a facility, and the effectiveness of various preventive measures. Reactivity monitoring is being used for the purpose of developing the cause-and-effect relationship between gaseous pollutants and the damage it may cause within preservation environments and to paper documents, artwork, and historical artifacts.

Air Purity Recommendations

Archives, Metal Collections, Rare Books:	**Class S1/C1**
Museums, Museum Storage, Libraries:	**Class S2/C2**
Historic Houses:	**Class S3/C3**
Short Term Acceptable:	**Class S4/C4**
Not Acceptable:	**Class S5/C5**

Generally speaking, the silver and copper corrosion rates should be Class S2/C2 or better, unless otherwise agreed upon. The individual corrosion films quantified using reactivity monitoring may be used to further characterize the environment and to determine the proper control

Table 4: Environmental classifications for preservation environments

Silver Corrosion: Class	Air Quality Classification	Corrosion Amount	Copper Corrosion: Class	Air Quality Classification	Corrosion Amount
S1	Extremely Pure	<40 Å / 30 days	C1	Extremely Pure	<90 Å / 30 days
S2	Pure	<100 Å / 30 days	C2	Pure	<150 Å / 30 days
S3	Clean	<200 Å / 30 days	C3	Clean	<250 Å / 30 days
S4	Slightly Contaminated	<300 Å / 30 days	C4	Slightly Contaminated	<350 Å / 30 days
S5	Polluted	≥300 Å / 30 days	C5	Polluted	≥350 Å / 30 days

strategies. Based upon these recommended control levels and test results from laboratory and field-exposed silver coupons, acceptance criteria relevant to these applications have been determined. These criteria take into account total corrosion, as well as the relative contribution of each individual corrosion film. The control specifications for the individual corrosion films are listed in Table 5. These specifications are more general in their application than those listed above, and are most often used for the characterization of an environment prior to the implementation of pollutant control measures.

As long as the total corrosion *and* each individual corrosion film meets the recommended criteria, the local environment in which that particular coupon has been exposed is deemed to be acceptable. *Any* of the criteria which are not met indicate that the local environment may not be sufficiently well-controlled to minimize the decay of artifacts and materials due to the presence of gaseous pollutants. Steps should be taken to determine what problems exist, and what corrective actions may be appropriate.

Summary and Conclusions

For the last several years, Purafil has been working with a number of institutions to develop and refine techniques with which conservators may accurately gauge the destructive potential of their environments toward those artifacts and materials entrusted to their care. However, no definitive information currently exists which describes the cause-and-effect relationship between specific levels of gaseous pollutants and the damage caused to artifacts and archival materials. Because of this, many are questioning the applicability and costs of direct gas monitoring and have turned to an alternate method of environmental classification: reactivity monitoring.

This environmental analysis method is currently being used by a number of museums and archives, and has been described in the literature. The validity for this air-monitoring technique lies in the fact that many of the contaminants which are of primary concern in preservation environments are corrosive in nature and, therefore, can be easily monitored via reactivity monitoring.

Standards have been proposed which directly correlate silver reactivity rates to environmental classifications, and these are being refined based on the results of testing and the specific needs of these environments. In fact, many new facilities or major renovations over the last several years have made reactivity monitoring a part of their overall environmental control strategy. Some of the more prominent examples of this are listed here.

- Environmental classifications using reactivity monitoring have now been adopted as standard for all Dutch government archives, as a result of extensive government-sponsored testing at the General Government Archives at The Hague.
- The Italian government required the use of reactivity monitoring in both the Sistine Chapel and Leonardo da Vinci's *Last Supper*, once restoration activities were complete. It sponsored a survey of all the major museums in Italy in order to evaluate the broad application of an environmental classification system based on reactivity monitoring. Reactivity monitoring has been performed at more than 160 locations in 28 institutions. A draft standard is being prepared for consideration.
- Reactivity monitoring was used in the Capital Museum, the Forbidden City Museum, the Shanghai Art Museum and many others prior to and during the 2008 Olympics in Beijing, China to assure the environment was safe for many delicate historical artifacts that had never previously been publicly displayed.
- New national archive facilities built in Singapore, China, and New Zealand have made reactivity monitoring part of their environmental control specifications.
- In the United States, reactivity monitoring has been used in the National Archives, Archives II, and the state archives of Arizona, Georgia, California, Minnesota, and Washington.

Through analysis of ERCs used in museums around the world, it has been shown that, in many parts of the industrialized world, outdoor air does not meet general or specific acceptance criteria with regard to the levels of gaseous pollutants. Many instances of indoor air quality being deemed "not acceptable" have also been identified. Once the need for controlling gaseous pollutants has been established, and control levels have been suggested, the air quality of the space to be protected still needs to be determined. This includes an assessment of the quality of the air inside a facility, as well as the quality of the air outside the facility.

Table 5: General reactivity monitoring acceptance criteria

Silver Reactivity Acceptance Criteria		Copper Reactivity Acceptance Criteria	
Silver Corrosion Reaction Products	**Corrosion Film Thickness**	**Copper Corrosion Reaction Products**	**Corrosion Film Thickness**
Silver Chloride, $AgCl$	0 Å / 30 days	Copper Sulfide, Cu_2S	0 Å / 30 days
Silver Sulfide, Ag_2S	<50 Å / 30 days	Copper Oxide, Cu_2O	<150 Å / 30 days
Silver Oxide, Ag_2O	<50 Å / 30 days	Copper Unknowns	0 Å / 30 days
Total Silver Corrosion	**<100 Å / 30 days**	**Total Copper Corrosion**	**<150 Å / 30 days**

The amount of corrosion forming over any given period is a primary indicator of how well-controlled an environment may be. Where gas filtration is employed to maintain the interior concentrations of gaseous pollutants as low as possible, reactivity levels well within the general and specific acceptance criteria can be easily attained. It is felt that, if an environment exhibits a reactivity rate of S1/C1 (<40 Å and <90 Å / 30 days, respectively), there is nothing else that can be done, economically, to improve the environment. If the general reactivity monitoring acceptance criteria of S2/C2 is met, it is accepted that this is an environment sufficiently well-controlled as to prevent the decay/deterioration of objects and artifacts.

The monitoring results for those coupons which meet these criteria indicate that the local environment is deemed generally acceptable for the conservation/preservation of historical artifacts and archival materials.

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Chris Muller is Technical Director of Purafil Inc.