PRACTICAL APPLICATIONS OF REACTIVITY MONITORING IN MUSEUMS AND ARCHIVES



Considerations for Monitoring and Classification of Gaseous Pollutants

> Purafil, Inc. 2654 Weaver Way Doraville, Georgia 30304 USA

PRACTICAL APPLICATIONS of REACTIVITY MONITORING in MUSEUMS & ARCHIVES

CONSIDERATIONS FOR MONITORING AND CLASSIFICATION OF GASEOUS POLLUTANTS

Chris Muller • Purafil, Inc.

TABLE OF CONTENTS

SUMMARY	 	Page 1
INTRODUCTION	 	<u>Page 1</u>
AIR MONITORING TOOLS AND TECHNIQUES	 	Page 2
Direct Gas Monitoring	 	Page 2
Reactivity Monitoring		
Corrosion Classification Coupons (CCCs)	 	Page 3
Environmental Reactivity Monitors (ERMs)	 	Page 4
CONTROL SPECIFICATIONS	 	Page 5
Environmental Classifications		
PURAFIL'S MUSEUM DATABASE	 	Page 7
Results and Discussion	 	Page 7
General Reactivity Monitoring Results.	 	Page 7
Geographic Comparisons.		
Comparison of Outdoor and Indoor Air Quality		
Comparisons Between Facility Types.		
Measurement of the Effectiveness of Gas-Phase Air Filtration Systems		
SUMMARY & CONCLUSIONS	 	Page 9
REFERENCES	 	Page 10

LIST OF TABLES

Table 1 - Currently available real-time chemical/gas monitors	Page 3
Table 2 - Control specifications for preservation environments	Page 5
Table 3 - Environmental classifications for preservation environments	Page 6
Table 4 - General reactivity monitoring acceptance criteria	Page 6

LIST OF FIGURES

Figure 1 - Corrosion classification coupon	Page 4
Figure 2 - Quartz crystal microbalance	Page 4
Figure 3 - OnGuard 2000 Environmental Reactivity Monitor	Page 4
Figure 4 - OnGuard Continuous Corrosion Transmitter	Page 5
Figure 5 - Chemical filter efficiency monitoring	Page 8
Figure 6 - Chemical filter performance monitoring	Page 9

Practical Applications of Reactivity Monitoring in Museums and Archives Considerations for Monitoring and Classification of Gaseous Pollutants

Chris Muller

Technical Services Manager

Purafil, Inc.

SUMMARY

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. 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. 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.

Active sampling using activated carbon (permeation) tubes can quantitatively collect volatile organic compounds (VOCs) and provide the high accuracy and precision necessary for detecting small changes in VOC concentrations. This method, however, is not applicable for monitoring of many of the chemical compounds which are of primary concern in libraries and archives. Specifically, this method cannot be used for formaldehyde and many inorganic compounds such as sulfur and nitrogen oxides, ozone, chlorine, or hydrogen chloride.

For the past 10 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 materials and artifacts entrusted to their care. As time went on, this undertaking split along two paths. The first involved the evaluation and development of monitoring tools and techniques that could accurately assess local environmental conditions. The second was the formulation of a classification scheme that would allow conservators to determine if their environments were truly "preservation environments" or whether pollutant control measures were indicated.

Based on joint research performed by Purafil, the governments of the Netherlands and Italy, and the Swedish Corrosion Institute, environmental monitoring using either silver or copper reactivity (corrosion) monitoring has been accepted as an alternative to, and in many instances preferred over, direct monitoring of low-level gaseous pollutants for performing environmental assessments. Monitoring devices have been developed and refined and standard classifications have been instituted which directly correlate copper and silver reactivity rates to environmental conditions.

INTRODUCTION

In libraries and archives 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 (SO₂), ozone (O₃), and nitrogen dioxide (NO₂). Others of primary concern include chlorides (chlorine [Cl₂] and hydrogen chloride [HCl]), acetic acid (CH₃COOH), and formaldehyde (HCHO).

While automotive and/or industrial emissions are considered as largest contributors of SO₂, O₃, NO₂, 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, building and display materials, and employees and patrons themselves can contribute to the overall pollutant load.

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 1990's.

There is some information, research, and consideration of common urban pollutants and their effects on artwork and archival materials, and 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 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 assure 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.

Active (Dynamic) Sampling. A common and relatively simple method of direct gas monitoring is through the use of sorbent tube samplers and a calibrated sampling pump. A known volume of air is drawn through an air sampling tube containing one or more adsorbent materials from which the sample is later thermally desorbed and introduced into a gas chromatograph (GC) or a gas chromatograph/mass spectrometer (GC/MS) for identification and quantification. Detection limits of $1 \mu g/m^3$ and below can be achieved.

Activated carbon is the most widely used sorbent material and it can be used to detect and quantify a wide range of chemical species. Multisorbent tubes containing materials such as Tenax[®] and/or Ambersorb[®] in addition to activated carbon can be used to collect an even broader range of chemical compounds. These air samplers can quantitatively collect chemical compounds spanning a broad range of boiling points, including highly volatile solvents.

Properly used, active sampling using sorbent tubes can (1) quantitatively collect volatile organic compounds (VOCs), (2) provide the high accuracy and precision necessary for detecting small changes in VOC concentrations, and (3) requires relatively low sample volumes making it adaptable to a variety of applications. This method cannot, however, be used to monitor many other chemical compounds which are of primary concern in libraries and archives. Specifically, this method cannot be used for formaldehyde and inorganic compounds such as sulfur and nitrogen oxides (SO₂, NO, NO₂), ozone (O₃), chlorine (Cl₂), or hydrogen chloride (HCl).

Although the use of carbon (charcoal) tubes or multisorbent tubes is an active sampling air monitoring technique, it is not a real-time monitoring method. Based on the expected concentration of materials in the air as well as the amount of sorbent material(s) contained in the sampling tubes, a relatively small volume of air is sampled. Thus, the chemical concentration reported is actually an average value over the sampling period.

Real-time Gas Monitoring. 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 - both organic and inorganic. 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.

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 Formaldehyde Hydrochloric acid Hydrogen sulfide Nitrogen oxides Ozone Sulfur dioxide TVOC	0-200 0-1000 0-200 0-200 0-200 0-1500 0-200 0-20,000	$ \begin{array}{c} 1.0\\ 0.2\\ 1.0\\ 1.0\\ 0.1\\ 1.0\\ 0.1\\ 20.0 \end{array} $	900 300 900 120 90 50 120 120	Medium High Medium Medium NO-High, NO ₂ -Low High High Low	Low Low High Low Low Low Low Low

To accurately gauge the destructive potential of an environment towards the materials stored within the space, one must be able to monitor for *all* of the contaminants of concern. Active sampling with sorbent tubes is really only applicable for monitoring organic compounds. Real-time chemical monitors can be used for these materials and many inorganic compounds, however, the use of two or more different monitors would be required. The ability to monitor all of the contaminants of concern at the desired levels will most likely require a combination of passive and active sampling techniques in addition to real-time monitoring. This quickly becomes a very expensive undertaking.

Reactivity Monitoring

Even though it is possible to identify and quantify essentially 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. Measurable levels of corrosion are indicative that corrosive attack can occur or may already be occurring.

Corrosion Classification Coupons (CCCs). CCCs (FIGURE 1) are passive monitors typically exposed to the environment for a period of 30-90 days and 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.

CCCs may be used to indicate the presence of SO_2 , O_3 , NO_2 , Cl_2 , HCl and many other materials which can cause deterioration of cellulose, organic materials, and metals. CCCs 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.

With this in mind, Purafil developed the use of silver reactivity monitoring for these unique environments. Silver is sensitive to chlorine and, when used with copper reactivity monitoring, can be used detect changes in the levels of gaseous pollutants in the ambient environment as small as 1 ppb and differentiate between different classes of contaminants.

The corrosion reported from reactivity monitoring with CCCs 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 (Cu₂S) and copper oxide (Cu₂O), respectively. For silver coupons, sulfide, chloride, and oxide films may be produced and are reported as silver sulfide (Ag₂S), silver chloride (AgCl), and silver oxide (Ag₂O), 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). The main limitation in the use of CCCs is their inability to provide a continuous environmental classification. To address this, Purafil has taken reactivity monitoring a step farther through the development of a realtime monitoring device employing metal-plated quartz crystal microbalances (QCMs, FIGURE 2).^{3,4} These microprocessorcontrolled 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 used in preservation environments.

To date, there is only one commercially available ERM employing copper and silver-plated QCMs which provides real-time information on the amount of corrosion occurring due to the presence of gaseous pollutants. The OnGuard[™] 2000 Atmospheric Corrosion Monitor (FIGURE 3) measures 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.

The OnGuard 2000 may be operated by independently, wired directly into a central computer system, or networked to relay information from multiple units to a central location. Monitoring data can be uploaded to a PC for viewing or graphing. By making use of the OnGuard's ability to interface with computers, 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.

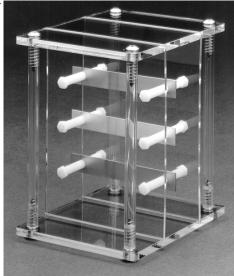


Figure 1 - Corrosion classification coupon



Figure 2 - Quartz crystal microbalance



Figure 3 - OnGuard 2000 Environmental Reactivity Monitor

The latest addition to Purafil's reactivity monitoring capabilities is the OnGuard Continuos Corrosion Transmitter (CCT, FIGURE 4). This device also employs QCMs to provide environmental reactivity data and transmits this information to a PC or control system via a 4-20 mA output signal. Cumulative or incremental corrosion rates can be logged, allowing for the detection and measurement of contamination episodes or events.

CONTROL SPECIFICATIONS

There is ongoing research to determine what levels of chemical contaminants actually cause deterioration of archival materials and historical artifacts.⁵ However, most experience has come from the 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 last fifty years than in the



previous two thousand. As stated earlier, it was not until the industrial Figure 4 - OnGuard Continuous revolution, and more distinctly, "the age of the car" that global pollutant Corrosion Transmitter levels dramatically increased.

The most commonly cited control levels for gaseous contaminants are shown in TABLE 2. Background concentrations and peak urban levels for these contaminants are also listed for comparison. As can be seen, the recommended levels for several contaminants are below the normal background levels and all are below contaminant levels we would expect to encounter in urban environments.

Table 2 - Control specifications for preservation environments						
Contaminant/Parameter Measured	Acceptable Level		Reactivity Level ⁶ ,	Normal	Peak Concentrations	
Measured	ppb	ug/m ³	Å/30 days	Background Concentrations		
Sulfur dioxide Ozone Nitrogen dioxide Chlorine	<0.35 - 1.0 <2.65 <0.94 - 12.5 <1 - 3	<1 - 2.85 <1.8 - 24.5 <5 <3 - 9		6 - 30 ppb 0.4 ppb 1.0 - 1.5 ppb 0.06 - 0.6 ppb	100 - 750 ppb 20 - 40 ppb 40 - 100 ppb 20 - 130 ppb	
Hydrogen chloride Acetic acid Formaldehyde	<1 - 3 <4 <4	<1.5 - 4.5 <10 <5	- -	20 - 50 ppb 4 - 10 ppb 3 - 15 ppb	200 - 450 ppb 20 - 100 ppb 10 - 40 ppb	
Silver Reactivity Copper Reactivity	-	-	$<\!\!100^{a} <\!\!150^{b}$	-	-	

a - with no chloride corrosion evident, b - with no sulfur corrosion evident

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, chlorine and ozone are to be removed completely. Other sources recommend levels from fractional parts-per-<u>billion</u> up to the low parts-per-<u>million</u>. 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. Whether or not the levels specified are realistic or attainable is another question.

Based on joint research performed by Purafil, Inc., the government of the Netherlands⁷, the Swedish Corrosion Institute⁸, and the Comitato Termotechnical Italiano (C.T.I.),⁹ reactivity monitoring using either copper or silver corrosion rates, has been accepted as a preferred alternative to direct monitoring of low-level gaseous pollutants in archives. It has become the standard for air quality monitoring in Dutch government archives and is being proposed as a European standard. These specifications are also shown in TABLE 2.

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.^{10,11} 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 <15-20Å / 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 2, there is little else that can be done, economically, to improve the environment.

Environmental Classifications. TABLE 3 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 archives and libraries. 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 to paper documents, artwork, and historical artifacts.

Table	Table 3 - Environmental classifications for preservation environments					
	Silver Corrosic	on		Copper Corrosion		
Class	Air Quality Classification	Corrosion Amount	Class		Corrosion Amount	
S1	Extremely Pure	<40Å / 30 days	C1	Extremely Pure	<90Å / 30 days	
S2	Pure	${<}100\text{\AA}$ / 30 days	C2	Pure	${<}150\textrm{\AA}$ / 30 days	
S 3	Clean	<200Å / 30 days	C3	Clean	${<}250\textrm{\AA}$ / 30 days	
S4	Slightly Contaminated	<300Å / 30 days	C4	Slightly Contaminated	<350Å / 30 days	
S5	Polluted	>300Å / 30 days	C5	Polluted	>350Å / 30 days	

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 strategies. Based upon these recommended control levels and test results from laboratory and field-exposed silver coupons, acceptance criteria relevant to these applications has 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 4. 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.

Table 4 - 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 Silver Sulfide, Ag ₂ S Silver Oxide, Ag ₂ O	0Å / 30 days <50Å / 30 days <50Å / 30 days	Copper Sulfide, Cu ₂ S Copper Oxide, Cu ₂ O Copper Unknowns	0 Å / 30 days <150Å / 30 days 0Å / 30 days	
Total Silver Corrosion	<100Å / 30 days	Total Copper Corrosion	<150Å / 30 days	

As long as the total corrosion <u>AND/OR</u> each individual corrosion film meets the recommended criteria, the area monitored is deemed to be acceptable. <u>ANY</u> of the criteria which are not met indicates that the environment may not be sufficiently well-controlled to minimize the decay of materials and artifacts due to the presence of gaseous pollutants. Steps should be taken to determine what problems exist and what corrective actions may be appropriate.

PURAFIL'S MUSEUM DATABASE

Purafil has taken reactivity monitoring results from museums, archives and libraries around the world and developed a database (categorized by facility type, location, etc.) which has been used to provide historical data. This database has proven to be a useful tool for comparing the performance of environmental control systems currently in place and for projecting improvements possible through the installation of gas-phase air filtration.

The ability to compare results with other museums and archives provides additional information to conservators on individual institutional performance. The museum database summarizes monitoring results from different locations within a facility as well as from different geographic areas and institution types. Summary results are presented below. A full description of the database results are available for review upon request.

Results and Discussion

To date, Purafil's Museum Database contains the analysis results for more than 1000 CCCs. Reactivity data has been obtained from at least 136 different institutions (facilities) in 16 countries around the world. In the U.S., reactivity monitoring has been used in 22 states. For ease of classification, the data has been categorized as coming from either a museum, archive, or library. Currently, there is data from 95 museums, 27 archives - including national and state facilities, and 14 libraries - including 4 national facilities. These results as well as differences between geographic areas and outdoor/indoor air is presented.

General Reactivity Monitoring Results. Coupons were classified as being exposed to outdoor air (either outside the facility or air being introduced to the building for ventilation purposes), indoor air, or inside museum cabinetry or display cases.

As expected, the outdoor air showed the highest level of corrosion. Indoor air exhibited corrosion rates approximately one-third those of outdoor air. CCCs exposed in cabinets exhibited the lowest average corrosion, although corrosion rates above the S3 level (>200 Å/30 days) were observed for 10% of the coupons.

Based on the environmental classifications and the air purity recommendations listed in TABLE 3, on average, outdoor air quality is generally not acceptable for these environments and treatment of this air may be indicated. As a minimum, continuous monitoring of the outdoor should be performed in order to make a determination regarding the implementation of a gaseous pollutant control strategy.

Geographic Comparisons. The database contains coupons which can be grouped into three geographic areas -Europe, North America, and Australia/South Pacific. The average total corrosion and the corrosion film breakdown for each country in the three geographic areas was determined.

Germany exhibited the highest average silver reactivity rate for the *European* group. It was approximately three times the group average of 170 Å/30 days. Three other countries - Italy, Sweden, and England - also exhibited reactivity rates higher than the European average. Of the 25 highest recorded reactivity rates for the entire database, all but five came from one of these four countries.

In the *North American/Carribean* group, only the outdoor air reactivity rates for the United States averaged slightly above Class S2 (111 Å/30 days). Of the 22 states, only 6 would have been classified S2 or better. The results from the heavily industrialized northeast region were generally lower than those from the agricultural midwest region. The west and the midwest had the highest average reactivity rates while the southeast exhibited the lowest.

For the *South Pacific* group, both Australia and New Zealand exhibited reactivity rates higher than S2/C2. Somewhat surprising was that New Zealand, which has little industry, had the highest average reactivity level. However, considering that this is an island country and that corrosion rates in seaside locations are generally higher than

locations further inland, this was not totally unexpected. The fact that chloride corrosion accounted for almost half of the total corrosion is a good indicator of the presence of atmospheric chlorine from seawater.

Comparison of Outdoor and Indoor Air Quality. The reactivity of the outdoor air was approximately three times higher than that of the indoor air. To provide an indication of where a particular facility's air quality is in relation to the entire database, a distribution of the results for outdoor air, indoor air, and the air inside of cabinetry is required.

- More than 80% of those locations where the coupons were exposed to outdoor air would be said to not meet the
 general acceptance criteria of S2/C2 and almost 40% of the locations would be considered as "not acceptable"
 (S5/C5).
- Only 35% of indoor locations did not meet the general acceptance criteria and only 5% would be considered "not acceptable."
- 87% of the cabinetry and display cases monitored would meet the general acceptance criteria with less than 2% being considered "not acceptable." However, if one looks at the cabinetry data for acceptability in housing metal collections, only 35% would be considered acceptable (S1/C1).

Based on the environmental classifications, for the vast majority of locations monitored, the outdoor air being used for ventilation purposes should be treated (filtered) prior to being introduced into a facility.

Comparisons Between Facility Types. The indoor air reactivity monitoring data was examined for the three different facility categories - museums, archives, and libraries. The acceptance criteria established for each facility type was Class S2/C2 for museums and libraries and Class S1/C1 for archives.

- For monitoring inside museums, the reactivity rate was considered acceptable ~60% of the time. Less than 5% of the locations would be considered as "not acceptable."
- For libraries, ~70% of the locations would have acceptable air quality. Less than 5% of the locations would be considered as "not acceptable."
- In archives, the lower acceptance criteria meant that the air purity recommendations were met in <30% of the locations monitored. Less than 2% of the locations would have been considered "not acceptable."

Measurement of the Effectiveness of Gas-Phase Air Filtration Systems. If it is accepted that gaseous pollutants are generally present in concentrations high enough to be problematic in preservation environments, then the most appropriate control strategy must be determined for the outdoor air, the indoor air, or both. The most effective and economical solution is provided by the use of a gas-phase air filtration system employing one or more dry-scrubbing media such as Purafil Select Chemisorbant, Purakol brand activated carbon, and/or Puracarb PP-1505.^{12,13} Once such a system has been installed and is in operation, one must be able to ascertain its performance relative its operating (performance) criteria.

Reactivity monitoring is well-suited for this task. Monitors placed upstream and downstream of the chemical filters can provide information on the effectiveness of the system. Reactivity monitoring can also be used to gauge media life so media changeout dates can be reliably forecasted and replacement media budgeted.

FIGURES 5 and 6 show the type of data which can be obtained from the use of reactivity monitoring for chemical filtration performance. Figure 5 is from a museum using a Purafil gas-phase air filtration system to clean the outdoor air. CCCs were placed up- and downstream of the filtration system to provide an indication of the filter efficiency. Each set of coupons was left in place for 90 days and then replaced with a new set. Data for three set of coupons is shown.

Figure 6 shows data from an archival facility employing a Purafil system. There was a concern about chlorine from a nearby cooling tower being introduced into the facility through the outdoor air intakes, so silver coupons were placed up- and downstream of the chemical filters. This time the main purpose of the reactivity monitoring was to determine if the chemical filters were removing the chlorine. By providing a breakdown of the individual corrosion films, it can be seen that the chlorine had been completely removed - indicated by the absence of a silver chloride film in the downstream sample. The overall environmental classification went from an S5 to an S1.

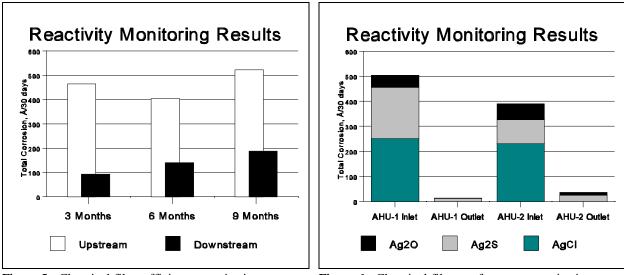


Figure 5 - Chemical filter efficiency monitoring



SUMMARY & 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 causeand-effect relationship between specific levels of gaseous pollutants and the damage caused to archival materials and artifacts. Because of this, many are questioning the applicability and costs of direct gas monitoring using active sampling and/or real-time 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 archives and libraries, and has been described in the literature. The validity for this air monitoring technique lies in the fact 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 classifications have been developed 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.

- The Italian government required the use of real-time reactivity monitoring in both the Sistine Chapel and Leonardo da Vinci's "Last Supper" once restoration activities were complete. Real-time reactivity monitoring is also being used in the Biblioteca de Brera. A survey of all the major museums in Italy was performed 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.
- 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.
- 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.
- New national archive facilities built in Singapore and New Zealand have made reactivity monitoring part of their environmental control specifications.

Through the analysis of Purafil's Museum Database, it has been shown that in many parts of the industrialized world, outdoor air does not meet general or specific acceptance criteria with regards 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 as well outside the facility.

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 reactivity rate of S1/C1 (<40Å and <90Å / 30 days, respectively), there is nothing else which 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 and/or deterioration of objects and artifacts.

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

REFERENCES

- 1. Abbott, W.H., "The Effects of Operating Environments on Electrical and Electronic Equipment Reliability in the Pulp and Paper Industry,"*IEEE Conference Record*, Institute of Electrical and electronic Engineers, Inc., New York, 1983.
- 2. Rice, D.W., et al., "Atmospheric Corrosion of Copper and Silver," *Electrochemical Society*, 128(2), pp 275-284, 1981.
- W.G. England, et al., "Applications of a Real-Time Electronic Contact Corrosion Monitor," *Proceedings of Advances in Instrumentation and Control*, Vol 46: pp 929-955, Instrument Society of America, Anaheim, 1991.
- 4. A.J. Weiller, "Electronic Monitoring of Indoor Atmospheric Pollutants," *Proceedings of Healthy Buildings* '94, pp 241-243, National Coalition on Indoor Air Quality, 1994.
- 5. Steemers, T., "The Delta Plan: From Policy to Practice," National Archives, The Netherlands, June, 2000.
- 6. Muller, C.O. 1996. "Airborne Contaminant Guidelines for Preservation Environments," *Proceedings of the* 24th Annual Meeting, American Institute for Conservation of Historic and Artistic Works, Washington, D.C..
- 7. "Advisory Guide-Line Air Quality Archives," *Delta Plan for Culture Preservation* Ministry of Housing, Spatial Planning and the Environment, Government Buildings Agency, The Hague, The Netherlands, 1994.
- 8. M. Forslund, *A Quartz Crystal Microbalance Probe for in situ Atmospheric Corrosion Monitoring* Department of Materials Science and Engineering, Division of Corrosion Science, Royal Institute of Technology, pp. 1-44, Stockholm, 1996
- 9. "Microclima, Qualità Dell'Aria E Impianti Negli Ambienti Museali," Giornata Seminariale, Associazione Italiana Condizionamento dell'Aria Rescaldamento, Refrigerazione, Firenze, Italy, pp 39-66, February 1997.
- 10. Muller, C.O., "Gaseous Contaminant Control Strategies at the Hague," *Proceedings of the 87th Annual Meeting*, Air & Waste Management Association, Pittsburgh, PA, June, 1994.
- Muller, C.O., "Airborne Contaminant Guidelines for Preservation Environments," *Proceedings of the 24th* Annual Meeting, American Institute for Conservation of Historic and Artistic Works, Washington, D.C., June, 1996.
- 12. Muller, C.O. and England, W.G., "Gas-Phase Air Filtration: Single Media or Multiple Media Systems. Which Should Be Used for IAQ Applications?," *Proceedings of IAQ '94: Engineering Indoor Environments*, American Society of Heating, Refrigerating, and Air-Conditioning Engineers, St. Louis, 1994.
- 13. Muller, C.O. and England, W.G., "Achieving your Indoor Air Quality Goals: Which Filtration System Works Best?," *ASHRAE Journal*, pp. 24-32, February 1995.