The Getty Conservation Institute

# Monitoring for Gaseous Pollutants in Museum Environments

# **FOR CONSERVATION**

Cecily M. Grzywacz

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The Getty Conservation Institute works internationally to advance conservation and to enhance and encourage the preservation and understanding of the visual arts in all of their dimensions—objects, collections, architecture, and sites. The Institute serves the conservation community through scientific research, education and training, field projects, and the dissemination of the results of both its work and the work of others in the field. In all its endeavors, the Institute is committed to addressing unanswered questions and promoting the highest possible standards of conservation practice.

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Pollutant Damage to		
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Since its inception, the Getty Conservation Institute has been committed to preventive conservation and the care of collections. Its earliest scientific endeavors focused on air pollution and its effects on collections, including monitoring pollutant levels in museums, the effects of pollutants on artists' materials, protection of works of art from pollution, and modeling of pollutant distributions in galleries. The results of this research were disseminated to the museum conservation community through various conservation and scientific journals as well as through conservation courses developed and presented by the GCI's Training Program. These courses took place between 1991 and 1996 in North America, the United Kingdom, and Latin America. A component of the courses dealt with environmental issues, including gaseous pollution and the risk it posed to collections. After participating in the course, Cecily Grzywacz helped to extend the GCI's environmental research by exploring ways in which museums could monitor for gaseous pollutants with passive sampling devices. This further developed into the creation and testing of protocols for extracting valid, statistically viable data from these devices.

This book is the synthesis of Cecily Grzywacz's years of work in testing museum environments. What began as a literature review on the effect of air pollution on materials in the conservation and scientific fields—with a section on air quality monitoring—has evolved into a handbook on air quality monitoring for museum environments. Although Cecily has shared her findings over the years with many museum professionals, this publication makes air quality monitoring available to a wider audience, not only those in museums, but also in the larger community of cultural resources managers responsible for collections.

Monitoring for Gaseous Pollutants in Museum Environments is the first book to specifically address air quality monitoring in galleries, storage areas, display cases, and storage cabinets. The methodology it presents can be implemented without an extensive scientific background. It is our hope that it will give professionals the necessary tools to understand the risk of gaseous pollutants to various collections and to conduct their own air quality monitoring studies.

Timothy P. Whalen Director The Getty Conservation Institute

"Telemachus, we must get the armour together and take it down inside. Make some excuse when the suitors ask you why you have removed it. Say that you have taken it to be out of the way of the smoke, inasmuch as it is no longer what it was when Ulysses went away, but has become soiled and begrimed with soot."

Homer, The Odyssey, Book XIX (800 B.C.E)

In its broadest sense, a *pollutant* is a substance that has a detrimental effect on the environment or on something of value (including health) and is present in the atmosphere in amounts greater than natural concentrations, primarily due to human activity. Cultural property inside museums can be threatened both by outdoor pollutants, such as gases from car exhaust that make their way into buildings, and by pollutants generated from sources within museums, such as fumes from cleaning products. In most situations, indoor-generated pollutants pose a greater risk to collections than outdoor-generated pollutants. Typically, this is because the indoor source is in close and continuous proximity to objects. A wide range of materials, from textiles and works of art on paper to pigments and leather bindings, are at risk of damage from gaseous pollutants.

Damage to collections has been observed and documented since antiquity. One of the oldest writings may be Homer's description of protecting armor from soot. However, the link between object damage and air pollution was not always recognized. In 1965 Thomson wrote one of the first works in conservation literature on contamination in museums: "Air Pollution: A Review for Conservation Chemists." The increasing awareness of the effects of air pollution on cultural heritage was elaborated by Thomson in *The Museum Environment* (2d ed. 1994).

In the late 1980s studies were undertaken on the concentrations of gaseous pollutants in museums and libraries. Since that time air pollution research has continued by conservators, conservation scientists, universities, governmental agencies, and industry. Most important, the risk of indoor-generated gaseous pollution was identified and investigated. This body of research led to the publication of several books. Hatchfield's *Pollutants in the Museum Environment: Practical Strategies for Problem Solving in Design, Exhibition, and Storage* (2002) was the first book to be dedicated to this topic. It presents conservators' concerns and discusses materials testing and mitigation methodologies. However, it

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does not discuss monitoring. Tétreault followed with an impressive literature review on air pollution, *Airborne Pollutants in Museums*, *Galleries and Archives: Risk Assessment*, *Control Strategies and Preservation Management* (2003a), which covers materials damage extensively. It applies risk assessment and preservation management tools developed by Michalski and Waller to air pollution in museum, galleries, archives, and libraries (Michalski 1990, 1993, 1996, 2000, 2002; Waller and Michalski 2004, 2005). And now, this book, *Monitoring for Gaseous Pollutants in Museum Environments*, provides necessary information to determine if pollutants are present and, if so, their concentrations.

This book is a synthesis of my twenty years of air quality monitoring research. My goal is to provide the most current information on detecting gaseous pollutants that are a risk to collections for conservators, collection managers, curators, registrars, and private collectors. Passive sampling techniques are the focus of this book because they are relatively inexpensive, easy to use, and readily available.

Chapter 1 provides an overview of the history and nature of pollutants of concern to museums and explores the challenges for scientists, conservators, and collections managers in developing target pollutant guidelines to protect cultural property. Although some pollutants are particles, this book focuses on gaseous pollutants, since they are impossible to see or detect without air quality monitoring and thus can attack objects for a long time before actual damage becomes visible. The photo essays in chapter 2 illustrate the damage that these gaseous pollutants can cause. Chapter 3 discusses the criteria for using passive sampling devices in museum environments. The products currently available to the conservation field are presented in chapter 4; tables 4.2 through 4.5 present detailed information on the various types of samplers.

The development of an air quality monitoring program is covered in chapter 5. Here I stress the importance of defining the objective of the testing for pollutants; for example, is it necessary to quantify pollutant concentrations, or is the absence or presence of a particular gas sufficient information? Appropriate planning maximizes precious fiscal and staff resources. Chapter 6 discusses what to do with the results obtained, both in terms of understanding the numbers and in terms of eliminating or minimizing the risk from gaseous pollutants. Ultimately, what is important is using the results of air quality monitoring for the preservation of the collections.

Chapter 7 describes the implementation of the information presented in this book in an extensive air quality monitoring program undertaken at the J. Paul Getty Museum at the Getty Center from 1996 to 1998.

Appendix 1 is the primary reference. It is a comprehensive compilation of the major gaseous pollutants that museum professionals may encounter, their sources, and the at-risk materials. As a guideline, current risk concentrations for the key gaseous pollutants are presented in Appendix 2 as a data interpretation reference. This is based on current knowledge and is subject to change as we learn more. Selected materials'

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tests, along with references, are listed in Appendix 3 to enable the selection of appropriate materials for use in proximity to objects. Finally, protocols for the preparation and analysis of two types of PSDs are provided in Appendix 4. A selected bibliography on damage to museum collections by gaseous pollutants follows the references at the end of the book.

It is my hope that this book will provide greater appreciation for the silent and usually long-term attack of gaseous pollutants.

Many scientists and museum professionals have been integral to my work over the years. Through my initial research on indoor-generated pollutants, I met Norman Tennent, a private conservation scientist based in Glasgow, Scotland; our collaboration led to the investigation of locations with visible damage from pollutants. Norman introduced me to many scientists, conservators, and collection managers, all of whom added to my body of knowledge. Most important, he introduced me to Lorraine Gibson, who was then completing her Ph.D. at the University of Strathclyde. Lorraine and I collaborated for several years on the evaluation of passive samplers for the conservation field. Soon we joined forces with Agnes Brokerhof of the Netherlands Institute for Cultural Heritage (ICN) to conduct research on the detection of organic carbonyl pollutants. In 1998, what started out as a meeting to discuss our research became a two-day conference, "Museum Pollution: Detection and Mitigation of Carbonyls." More than thirty delegates from the United Kingdom, the Netherlands, Denmark, Canada, and the United States attended. From this conference, the Indoor Air Pollution Working Group was initiated. In particular, I would like to acknowledge the contributions of the following members of this group: Morten Ryhl-Svendsen, National Museum of Denmark; Jean Tétreault, Canadian Conservation Institute; Maarten van Bommel, ICN; and Simon Watts, Oxford-Brookes University. Over the years I have had the opportunity to work with several laboratory assistants who contributed to the GCI's environmental research, including Kristina Chadwick, Andrea Gailunas, Karen McKabney, Leo Perry, and especially Gisela Brock, who always knew what I wanted and needed before I finished my requests.

I have pursued pollution monitoring to assist conservators, collection managers, registrars, curators, museum professionals, and facilities managers and engineers with their questions and concerns about indoor air quality in display and storage areas. I am indebted to them for their interest and encouragement. In particular, I would like to thank Brian Considine, John Donohoe, Pamela Hatchfield, Abby Hykin, and Jerry Podany. There are many others; I wish there was sufficient space to recognize all of them.

I would be remiss not to recognize my GCI colleagues from 1985 to present. In the Science Department, I want to thank Frank Preusser for hiring me as an analytical chemist; Dusan Stulik for his

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Many passive sampling device vendors, analysts, and researchers took the time to discuss and understand the issues of air pollution in museums. Don Schaeffer and the board of Ogawa & Co., USA, Inc., were especially helpful.

Elizabeth Maggio, a highly skilled editor, was instrumental in tightening my original manuscript. We worked well together and learned from each other. I also wish to acknowledge the efforts of Cynthia Godlewski, GCI senior project manager, and the J. Paul Getty Trust Publications team: Ann Lucke, managing editor; Pamela Heath, production coordinator; Sheila Berg, project editor; and Gary Hespenheide, designer.

#### Gaseous Pollutants in Museum Environments: Overview

#### Air Pollution

Contaminated air is not just a phenomenon of modern times. It is easy to imagine that in the prehistoric era, smoke from cave fires obscured the details of art applied to cave walls. During Roman and medieval times in Europe and China, copper smelting produced prodigious amounts of airborne pollutants that were eventually deposited in Greenland (Hong et al. 1996). The vibrant colors of Michelangelo's wall paintings in the Vatican's Sistine Chapel were dulled by smoke from centuries of burning candles.

Beginning with the industrial revolution, the health threat caused by air pollution increased tremendously. By the mid-1900s, notable episodes of poor air quality brought pollution concerns to world attention. In 1952, for example, thousands of people died in London during five days of acute levels of smog. Four years earlier, sulfur dioxide emissions from industrial plants near Donora, Pennsylvania, had sickened 40 percent of the population and killed twenty people and many animals. In the United States, such disasters led to the enactment of legislation, most important, the Clean Air Act of 1990 (U.S. EPA OAR 1990).

Today, photochemical smog is a common occurrence in major metropolitan areas such as Los Angeles, Mexico City, Houston, and London.<sup>1</sup> But air pollution is no longer localized in large urban or industrial centers. Global wind currents can spread pollution far from its sources, resulting in regional pollution (Millan et al. 1996a). Gases detected in remote areas have been linked to vehicles and industries many kilometers away (Granby and Christensen 1997; Jaffe et al. 2003). Even areas once considered pristine now have serious air quality problems, such as Grand Canyon National Park in Arizona and Yosemite National Park in California (Kleiner et al. 2000; U.S. National Park Service, Air Resources Division 2005).

However, there are encouraging trends in air quality control in Western industrialized nations. Strict air quality regulations and pollution control innovations such as the catalytic converter for automobiles have resulted in measurable pollution abatement,<sup>2</sup> despite increases in the number of people, cars and trucks, and industries. Air quality can be expected to improve with further reliance on hybrid and alternative-fuel vehicles. In addition, the use of high-grade fossil fuels has dramatically decreased levels of sulfur dioxide in the United States, Canada, and Europe (Cape, Fowler, and Davison 2003). In some regions of the United States, sulfur dioxide levels have dropped so low that local air quality

agencies are no longer required to monitor for this pollutant. This is true for most of Southern California, especially in the Northwest Coastal Region, where both the J. Paul Getty Museum at the Getty Center and the J. Paul Getty Museum at the Getty Villa are located (SCAQMD 2002). On the other hand, newly developing countries are producing high concentrations of pollutants such as sulfur dioxide because of their increasing use of poor-grade fuels (Blanchard 1992; Chuang et al. 1992; Gorman 2000).

#### Outdoor-generated versus Indoor-generated Pollutants In Museums

In the outdoors, pollution is a function of climate, geography, the number and type of industries and vehicles, the fuel used, and so on. For instance, an island may have good air quality in spite of high vehicular and industrial emissions because pollutants are blown out to sea and diluted, whereas land-locked cities or those in basins, such as Los Angeles, tend to have poor air quality. Warm climates have higher concentrations of outdoor-generated pollutants (Millan et al. 1996b). Geography and temperature inversion layers can trap pollutants for days or weeks (Manahan 1994; Wilbraham et al. 1993), producing the familiar orange-brown haze of photochemical smog over major urban centers.<sup>3</sup> Schwab et al. (1993) report on seasonal and yearly trends.

Outdoor pollutants can enter a building, especially a naturally ventilated building (Druzik 1991), and pose a risk to collections. Naturally ventilated buildings have indoor concentrations of pollutants that are nearly equal to the outdoor levels. However, buildings with heating, ventilation, and air-conditioning (HVAC) systems that have gas-phase filtration minimize the infiltration of pollutants, reducing the indoor level to as low as 5 percent of the outdoor concentration. The major outdoor pollutants that are found inside museums and that pose a risk to cultural property are sulfur dioxide, nitrogen dioxide, nitrogen oxide, ozone, and reduced sulfur gases such as hydrogen sulfide.

The most common indoor-generated gases that pose a serious risk to cultural property are acetic acid, formic acid, acetaldehyde, formaldehyde, hydrogen sulfide, carbonyl sulfide, and ozone. Inside museums, these pollutants can be off-gassed from paints, boards, carpets, and cleaners, as well as many other materials and products. They can also be generated during such processes as cooking, cleaning, and heating. Cigarette smoke is a source of formaldehyde and other toxic compounds (Moree-Testa and Saint-Jalm 1981); whereas smoking in museums is heavily restricted in the United States, this is not always the case elsewhere in the world. The amount of a given pollutant that is generated depends on the nature of the source materials (Andersen, Lundqvist, and Mølhave 1975), the kinds and intensity of indoor activities (Chuang et al. 1992), and the efficiency of air-exchange and ventilation systems. Of course, many other gases-acetone, limonene, carbon dioxide, hexaneare generated indoors, but, fortunately, most of these volatile organic compounds do not damage collections.

Some pollutants of concern to museum collections can be generated both indoors and outdoors. For example, ozone, a major constituent of photochemical smog that forms outdoors, can also be produced indoors by air purifiers (U.S. EPA OAR 1998) and dry-process photocopiers (Brown 1999). Formaldehyde is typically associated with indoor pollution, especially from consumer products (Kelly, Smith, and Satola 1999) such as plywood and other composite boards (Andersen, Lundqvist, and Mølhave 1975). But levels of outdoor-generated formaldehyde and related compounds are increasing, especially from the use of alcohol-based fuels, as documented in several studies (Anderson et al. 1996, 1999; Anderson and Lanning 1999; de Andrade, Miguel, and Seinfeld 1999; de Andrade, Pinheiro, and Andrade 1995; Tanner et al. 1988; Yano, Ito, and Takehata 1986).

#### Gaseous Pollutant Terminology

For the most part, the chemical terms used in this book and listed on devices used to monitor air quality are straightforward: ozone, sulfur dioxide, nitrogen oxides, hydrogen sulfide. These are individual chemical compounds. However, certain pollutants belong to two classes of chemicals whose terms are often encountered in monitoring air quality, volatile organic compounds (VOCs) and organic carbonyl compounds.

#### Volatile Organic Compounds

VOCs are hydrocarbons that exist as gases at ambient temperatures and are generated both indoors and outdoors. Hundreds of VOCs can be detected inside nearly all buildings because they off-gas from a wide variety of sources: construction materials, solvent-based paints, primers, varnishes, aerosol sprays, cleaners, and disinfectants. Even the breath and perfume of museum visitors are sources of VOCs. The level of all VOCs in a building is, in a broad sense, indicative of overall air quality. Some pollutant monitors specifically detect all VOCs and average them into one number, called total VOCs, which is based on the calibration for a specified VOC gas, for example, hexane or toluene. With one notable exception, VOCs have not been linked to materials damage.

#### **Organic Carbonyl Pollutants**

Although many VOCs contain carbonyl groups, the organic carbonyl pollutants of primary concern to museums are formaldehyde and acetaldehyde (referred to collectively as aldehydes) and formic acid and acetic acid (organic acids). All four organic carbonyl pollutants are primary pollutants off-gassed from a source. In addition, acetic acid and formic acid can be secondary pollutants formed from the oxidation of acetaldehyde and formaldehyde, respectively.

#### Monitoring for Gaseous Pollutants in Museums

One of the goals of preventive conservation is to diminish pollution's risk to cultural property by minimizing the penetration of outdoorgenerated contaminants into buildings and by reducing sources of

pollutants generated indoors. Reaching this goal begins with adequate monitoring of the indoor air quality in museum environments. Here, "monitoring" refers to the determination of the presence of gaseous compounds in air that may damage collections, either directly or through conversion to secondary products.

Interest in museum environments can be traced to 1899, when Loftus St. George Byne published what is believed to be the first documented report of damage to collections from storage conditions (Byne 1899). Byne described the corrosion of shell specimens but wrongly attributed the cause to the decaying animal inside them. In fact, the corrosion is caused by acid vapors released from certain types of wood used for storage and display. Despite Byne's misinterpretation of what was happening to the shells, the damage is still referred to as Byne's Disease (Byne's Efflorescence is a more appropriate term because this is not a disease that spreads to other objects). Since then, an increasing number of accounts of materials damage from gaseous pollutants have been published (see Selected Bibliography).

Since the early 1970s, the number of reports of damage to museum collections has increased. In 1987 the publication of *Formaldehyde: How Great Is the Danger to Museum Collections?* (Hatchfield and Carpenter 1987) drew international attention to the problem posed by this organic carbonyl pollutant.

In 1985 the Getty Conservation Institute (GCI) began the first major, long-term research program into the risks posed to museum collections by atmospheric pollutants (Preusser and Druzik 1989). The initial focus was on outdoor pollutants that enter museums, such as nitrogen oxides, ozone, and sulfur dioxide. The research program later expanded to include indoor-generated pollutants, especially organic carbonyl pollutants (e.g., formaldehyde, acetaldehyde, formic acid, and acetic acid), which are potentially devastating for cultural material (Grzywacz 1989).

The first GCI investigation, from 1986 to 1989, involved seventeen museums in the United States. Samples collected from galleries, storage rooms, display cases, and storage cabinets revealed that high levels of aldehydes correlated with construction materials, a finding supported by earlier research that showed a connection between formaldehyde pollution and pressed board used in mobile home construction (Norsted, Kozinetz, and Annegers 1985; Pitts et al. 1989; Stock et al. 1985; U.S. EPA 2001).

The lowest concentrations of pollutants were detected in areas with good ventilation and high air circulation, such as galleries and artifact storage rooms. The highest concentrations were found in display cases or storage cabinets, where air circulation was restricted, allowing pollutants to build up over time. Of the four organic carbonyl pollutants, formaldehyde was present in the highest concentration in the majority of the nearly six hundred locations sampled. This study illustrates why museums should select construction materials carefully. (See Appendix 3.)

In 1993 the GCI conducted another air quality monitoring study to determine if it was possible to correlate pollutant concentration with materials damage. Sites were selected in the United Kingdom and the Netherlands that had collections damage thought to be attributable to organic carbonyl pollutants. Higher concentrations of organic carbonyl pollutants were detected in areas with damaged objects. And, more important, acetic acid was the predominant pollutant (Grzywacz and Tennent 1994; Tennent and Grzywacz 1993). This supported the hypothesis that organic acids are the attacking species.

From 1996 to 1998, the GCI collaborated with the J. Paul Getty Trust Facilities Department and the J. Paul Getty Museum Decorative Arts and Sculpture Conservation Laboratory to study the indoor air quality of the J. Paul Getty Museum at the Getty Center. Air quality monitoring was conducted during the final phases of construction, art installation, opening ceremonies, and the first few months after opening. This monitoring program is described in chapter 7.

In 1998 the GCI Science Department and the J. Paul Getty Trust Facilities Department began another study of the air quality in the J. Paul Getty Museum at the Getty Center. This time the purpose was to track the service life of the HVAC system's gaseous filtration media.

Other museums have conducted air quality monitoring surveys as well. Brimblecombe et al. (1999) studied air quality at the Sainsbury Centre for Visual Arts in the United Kingdom. Eremin and Wilthew (1998) and Eremin and Tate (1999) evaluated the air quality at the new National Museum of Scotland. Camuffo et al. (1999, 2001) monitored several European museums to determine mitigation methodologies to improve the preservation of the collections. Their work and others can be found in the reports of the Indoor Air Pollution Working Group. Sturaro et al. (2003) conducted environmental monitoring at the Kunsthistoriches Museum in Austria.

### Challenges to Developing Standards for Pollutants in Museum Environments

When exposed to pollution, people are more resilient than is art. Living organisms have defense systems and are capable of limited self-repair in response to attack. For people, it is reasonable to assign threshold limits or maximum exposure levels to harmful pollutants. In contrast, any chemical reaction between a pollutant and an object causes damage to the object. Although the damage may be at the molecular level and not yet visible, irreversible chemical changes have occurred. This is one reason that pollutant monitors for use in museums require extremely low detection limits, typically on the order of parts per billion (ppb). These levels are two to three orders of magnitude lower than regulations established by the U.S. Department of Labor's Occupational Safety and Health Administration (OSHA), and in some cases the difference is even larger. For example, silver tarnishing by hydrogen sulfide occurs at the parts per trillion (ppt) level (Watts 2000), which is six orders of magnitude lower than the parts per million (ppm) range set by OSHA for humans.

Technological developments over the past twenty years have permitted detection of ever lower concentrations of gaseous pollutants more accurately and more precisely. However, the big question is, what do the numbers really mean in terms of setting limits to protect cultural property?

This is not an easy question to answer. To begin with, not enough is known about the chemical processes that lead to pollution

damage of cultural materials (see chap. 2). Also, many parameters contribute to an object's overall risk of damage from a gaseous pollutant, and they must be considered and accounted for when determining exposure standards. Pollutants attack materials to different degrees (see discussion of Byne's Disease, chap. 2 and fig. 2.5), which is a function of what the object is made of and the specific composition of those materials. The integrity of the object (e.g., the quality of the materials and the object's history and storage conditions) and environmental conditions (e.g., relative humidity and temperature), as well as past conservation treatments, all play a role in the overall risk of damage.

Furthermore, we cannot ignore synergy for indoor climates and microclimates: the risk of damage from a mixture of pollutants may not be simply the additive effect of the materials' risks to each pollutant (Brimblecombe 1999, 2000). The synergistic effects of specific pollutant combinations on several materials, including papers, metals, stone, clays, and calcareous materials, have been studied (Bradley and Thickett 1999a; Johansson 1990; Klumpp, Heitmann, and Schwuger 1993; Svensson and Johansson 1996). Because of these and the many other parameters that contribute to potential damage from pollutants, all-encompassing exposure standards are impossible to establish (Gibson 1999b).

Complicating the problem of setting pollutant standards for museums is the need to consider that pollutant concentrations are typically measured in environments where damage has already occurred. We do not know which pollutants were present at the onset of deterioration or their concentration, when the damage actually occurred, or how long it took to develop. Often the onset of damage is gradual and goes unnoticed, especially for objects in storage. When the damage is discovered, the cause may be misattributed to a current event, as was the case at the Kunsthistorisches Museum in Vienna (see sidebar "Monitoring in Action: Kunsthistorisches Museum").

The end result of an air quality monitoring program is the pollutant concentration at the time of sampling. Yet the link between that number and the risk to various materials in typical air compositions has not been fully researched and understood. This is an arduous task, one that is being undertaken by researchers seeking to quantify the risk presented to various materials.

#### **Current Target Guidelines for Indoor Air Pollutants**

The development of air pollution standards for museum use is an ongoing endeavor. Still, progress is being made on several fronts. For example, recommendations for indoor air pollutant standards developed by the GCI and the Canadian Conservation Institute were incorporated in the pollution guidelines included in the American Society for Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) chapter "Museums, Libraries, and Archives" in its *Applications Handbook* (Baker and Grzywacz 2003). These recommendations are reviewed every four years and revised accordingly; Grzywacz is the current coordinator of future revisions.<sup>4</sup>

In a continuing effort to establish limits for pollutants that pose a risk to cultural property, Tétreault adapted the No Observable

#### Monitoring in Action: Kunsthistorisches Museum

In January 1998 the new curator of the numismatic collection at the Kunsthistorisches Museum in Vienna surveyed the coins in preparation for a major exhibition to open the following December. The collection had been stored for two hundred years in beautiful wood cabinets, as is typical for coin and shell collections. During the survey, the curator noticed that many of the coins showed signs of corrosion, and the paper labels for individual coins had become discolored and brittle.

The museum hypothesized that the damage was linked to pollution—exhaust gases and photochemical smog—from tourist buses, especially those from former eastern bloc countries, which used lowgrade fuels and had inefficient or no emission controls. The coin cabinets were located in the director's naturally ventilated office. On warm days, the windows were opened to provide fresh air, allowing fumes from the many tour buses to infiltrate the room.

The Getty Conservation Institute was asked to participate in a three-day meeting of conservators, scientists, and museum personnel to look into the question of whether these pollutants were in fact responsible for the deterioration of the coins. The cabinets containing the coins were examined and found to be extremely well made. Each cabinet had outward-opening doors that formed a tight seal when closed. Inside were a series of drawers with no visible gaps between them. Given this construction, it was more likely that the damage was from internally generated pollutants than from infiltration of outdoor-generated pollutants.

The deterioration was consistent with damage from indoorgenerated organic carbonyl pollutants. The most obvious source was the wood, oak and a variety of other species, used to make the cabinets and drawers. Oak produces acetic acid, which poses great risk to metals, such as the old coins. The GCI also identified the fabrics and boards that line the bottom of the drawers, the wooden dividers, adhesives, and paper labels as possible sources.

The next step was to monitor the environment of a large sample of drawers from different cabinets using a direct-reading passive sampling device (A-D Strips<sup>™</sup> [Image Permanence Institute, Rochester, N.Y.]). This simple and inexpensive air quality monitoring protocol confirmed the presence of potentially damaging acids. This information allowed the Kunsthistorisches Museum staff to develop appropriate palliative measures for the coin collection (Griesser 1999; Grzywacz 1998).

Adverse Effects Level (NOAEL), which is widely used to set standards for pharmaceuticals and pesticides, for preventive conservation. "NOAEL" refers to the greatest concentration or amount of a substance, found by experiment or observation, that causes no detectable adverse effect. Tétreault combined experimental data with theoretical information and exposure time to develop a Low-Observable Adverse Effects Level (LOAEL) system to classify pollutant concentration levels based on the susceptibility of the materials and the length of exposure (Tétreault 2003).

Appendix 2 is a table of current target pollutant levels for museums derived from the best available sources. Because these recommendations are based on data from limited research, museums should use them as a guide to making their own decisions about what risks certain pollutants pose to materials in their collections. Updates may become available on the websites of the Indoor Air Pollution Working Group, GCI, and the Canadian Conservation Institute (see sidebar "Useful Websites"), as well as in literature available at Art and Archaeology Technical Abstracts' AATA Online, a comprehensive database of abstracts of literature related to the preservation and conservation of material cultural heritage.

Efforts by a small group of researchers collaborating on a study of organic carbonyl pollutants led to a two-day conference in 1998

#### **Useful Websites**

American Society for Heating, Refrigerating, and Air-Conditioning Engineers: http://www.ashrae.org/

Art and Archaeology Technical Abstracts (AATA Online): http://aata.getty.edu/NPS/

Canadian Conservation Institute: http//www.cci-icc.gc.ca/frameset\_e.shtml

Getty Conservation Institute: http://www.getty.edu/conservation/

Getty Conservation Institute report on research program on pollutants: http://www.getty.edu/conservation/science/pollutants/index.html

Indoor Air Pollution Working Group: http://iaq.dk/iap.htm

at the University of Strathclyde in Glasgow, Scotland. The conference focused specifically on acetic acid, formic acid, and formaldehyde, pollutants that pose a high risk to collections. More than thirty scientists, conservators, and collection managers from the United Kingdom, the Netherlands, Denmark, Canada, and the United States met to discuss the development of standard methods of analysis, the relationship between pollutant concentration and artifact damage, mitigation methods, and the need for practical air quality standards for museums (Gibson 1999b). This initiative resulted in the establishment of the Indoor Air Pollution Working Group, an informal, independent group of concerned scientists, conservators, and collections managers dedicated to keeping up with important issues and developments regarding indoor air quality in museums and archives.

The 1998 Glasgow conference marked the beginning of a serious commitment to air pollution research and to finding practical solutions for museums. Since then, regular conferences with an expanded pollutant agenda have been held at the Instituut Collectie Nederland (the Netherlands, 1999), Oxford Brookes University (U.K., 2000), the National Museum of Denmark (Copenhagen, 2001), the University of East Anglia (U.K., 2003), and the Institute of Atmospheric Sciences and Climate, Italian National Research Council (Italy, 2004).

Members of the Working Group have published a number of studies reporting ranges of pollutant concentrations (Andrew, Tétreault, and Waller 1993; Eremin 1999, 2000; Eremin and Wilthew 1998; Grzywacz and Tennent 1994; Tétreault 1992a; Tétreault, Sirois, and Stamatopoulou 1998; see also http://iaq.dk). However, additional fundamental research needs to be done before scientists can assign definitive standards for pollutants in museum environments.

#### Why Monitor for Pollutants in Museums?

Among the reasons for conducting air quality monitoring in museum environments are the following:

- Damage or risk to objects is suspected, and the cause may be pollution in the microenvironment, for example, inside a storage cabinet or display case.
- There may be a known pollution problem, and concentration data are required before management will allocate fiscal and staff resources to address it.
- Mitigation measures are scheduled to reduce known pollutants that pose a risk to a collection or an object. To evaluate the procedure's effectiveness, initial pollution levels need to be documented.
- A building's effectiveness at keeping outdoor-generated pollutants from entering is unknown. This can be tested by comparing measurements of the outdoor pollutants with what is found inside.
- Monitoring for pollutants can rule out an indoor air quality problem.

#### Levels of Monitoring

At times, monitoring the museum environment is needed only to determine if dangerous pollutants are present. At other times, more specific monitoring programs are needed to determine which pollutants are present and their concentrations. This is the difference between qualitative and quantitative monitoring.

Qualitative monitoring answers the question, is the environment putting objects at risk from gaseous pollutants? In this approach, metal coupons, such as silver, lead, copper, or bronze, are exposed to the questionable environment and watched for visible changes such as corrosion that would indicate a potential problem. A limitation of this test is that even if the air does not damage the metal coupons, one cannot be certain that it is safe for other kinds of cultural materials or objects. Ideally, the test samples should be similar to the materials of the objects or made from materials that are even more susceptible. One example is the use of blue-wool standards for measuring light exposure.

Qualitative monitoring can also determine the general classes of pollutants present in the environment. The class of pollutant—aldehydes, organic acids, sulfides, inorganic compounds—can be deduced by knowing how different test samples react in the presence of different environmental contaminants. For example, the presence of sulfides is inferred if silver coupons tarnish rapidly, and the presence of organic acids is indicated by the corrosion of lead coupons.

In contrast to qualitative monitoring, in which the effect of a class of pollutant is evaluated, quantitative monitoring measures the concentration of a specific gaseous pollutant. This information is needed to elucidate or suggest the most likely source, so that remediation actions can be evaluated and implemented. Similarly, knowledge of specific pollutant concentrations presents a more compelling argument to improve the air quality in the area.

#### **Types of Monitors**

Regulations imposed by OSHA and the Environmental Protection Agency (EPA) to protect people from exposure to high levels of dangerous pollutants in the workplace spurred innovation in air quality monitoring. This has resulted in new detection systems with museum-level sensitivity. Museum monitoring can be done with either an active or a passive system. An active system uses a pump to pull a sample of air into the monitoring device, whereas a passive system allows air to diffuse into the device naturally. My focus here is on passive monitoring because it is generally less expensive and easier to employ than is an active monitoring system. Chapter 3 introduces the general concept of passive air sampling, and chapter 4 describes the types of passive sampling devices available to monitor museum environments.

#### When to Monitor

Air quality monitoring in museums is conducted to determine if there is a gaseous pollution problem or risk. But how long and how frequently should monitoring be carried out? Should there be an ongoing monitoring program? The answers to these questions depend on the specific situation and objective and are explored in chapter 5.

#### **Prevention Conservation**

Pollutants modify or destroy susceptible surfaces, and, in the process, valuable information about cultural heritage can be lost forever. Unless changes are made to the environment that originally caused the damage, damage will continue and further conservation treatments will be necessary. Monitoring and mitigation go hand in hand. Chapter 6 explains how to interpret results and introduces mitigation considerations.

#### Notes

- 1. For a discussion of the history of air pollution as it pertains to the preservation of cultural properties, see Brimblecombe 1977, 1988, 1991; Brimblecombe and Stedman 1982.
- A catalytic converter reduces air pollution by converting two exhaust products into less damaging substances: it oxidizes hydrocarbons from unburned fuel to carbon dioxide and water, and, to a lesser extent, it converts nitrogen oxides to nitrogen and oxygen.
- 3. "Smog" is a term originally used by the British to describe the mixture of smoke and fog that dirtied air over London (*Oxford English Dictionary* 1989). Today, the term generally refers to photochemical smog produced when sunlight triggers chemical reactions between atmospheric gases and contaminants in vehicle exhaust and industrial emissions. An orange-brown atmospheric layer over a city is a telltale sign of photochemical smog.
- Comments and suggestions for the ASHRAE Application Handbook, chapter 21, "Museums, Galleries, Archives, and Libraries," should be sent to Cecily M. Grzywacz, cgrzywacz@getty.edu.

#### The Effects of Gaseous Pollutants on Objects

Most gaseous pollutants that are a risk to collections are easily converted to their acidic analogs under ambient temperature and relative humidity. Current thinking is that the acidic forms are the damaging compounds, making acid-sensitive materials especially vulnerable to the pollutants. This has been demonstrated for nitrogen oxides; their acidic analogs (nitrous acid and nitric acid) are the reactant species.

Although the process is less clear for aldehydes (formaldehyde and acetaldehyde), fundamental chemical reactions provide researchers with some clues. Often their deductions are confirmed by observation and monitoring (Bradley and Thickett 1999a, 1999b). Telltale compounds that can be traced to aldehydes have been identified in corrosion products on cultural materials, leading researchers to suspect that the following three-step scenario is taking place (see fig. 2.1): (a) an aldehyde (e.g., formaldehyde or acetaldehyde), perhaps off-gassed from construction materials used in a display case, contaminates the atmosphere; (b) the aldehyde is transformed into an organic acid (e.g., formic acid or acetic acid) by the addition of oxygen provided by an oxidant such as a peroxide or ozone; (c) the organic acid attacks the museum object chemically, losing its hydrogen in the process and leaving behind its anion (e.g., formate or acetate) that is identified in the corrosion products. In addition to this reaction, both formic acid and acetic acid can be emitted directly from materials and products.

What is *not* known is if the aldehyde is oxidized to the organic acid in the air or on the surface of the object. Chemically, the acid is a reactant in the corrosion or damage process, but this has not been verified experimentally, especially with respect to the organic carbonyl pollutants that are a threat to collections. Raychaudhuri and Brimblecombe (2000) are the only researchers who have investigated the correlation of oxidation of formaldehyde to formic acid and corrosion. Bradley and Thickett (1999a) observed that 5 ppm and 0.5 ppm formaldehyde, while corrosive to lead at 100% RH, was not corrosive when the relative humidity was 50%. Their premise is that the formaldehyde is not easily oxidized to the acid at ambient conditions. Others have reported corrosion related to organic carbonyl pollutants at elevated relative humidity, 60% to 75% (Brokerhof and van Bommel 1996).

The difficulty of elucidating the chemical processes underlying pollutant damage to museum materials was evident in the findings of the

#### Figure 2.1.

Organic carbonyl pollutant reaction pathway to corrosion product. Transformation of an aldehyde (a) into an organic acid (b) and finally into an anion or salt found in corrosion products (c). Aldehydes are a risk to collections because they are easily oxidized to carboxylic acids, which in turn damage objects. An aldehyde has a hydrogen atom next to the carbonyl carbon that is extracted in oxidation and replaced by an oxygen or a hydroxyl group, depending on the reaction conditions forming an organic acid. Oxidants can be strong, such as permanganate, or mild, such as hydrogen peroxide or even light.



#### Metals:

 $\text{Lead} + \text{acetic acid CH}_3\text{COOH} \rightarrow \text{lead acetate PbCH}_3\text{COO} \rightarrow \text{basic lead carbonate}$ 

Lead + formic acid HCOOH<sup>1</sup>  $\rightarrow$  lead formate PbHCOO

- Zinc + formic acid HCOOH  $\rightarrow$  zinc formate ZnHCOO
- $\begin{array}{l} \text{Bronze} \rightarrow \text{Sodium copper carbonate hydrate NaCuCO}_3 \cdot \text{H}_2\text{O} + \text{acetic acid CH}_3\text{COOH} \\ \rightarrow \text{Sodium copper acetate carbonate NaCu(CH}_3\text{COO})(\text{CO}_3) \end{array}$

#### Calcareous Materials:

- Calcium carbonate  $CaCO_3$  + acetic acid  $CH_3COOH$ 
  - $\rightarrow$  calcium acetate hemihydrate Ca(CH<sub>3</sub>COO)·1/2 H<sub>2</sub>O
  - $\rightarrow$  calcium acetate hydrate Ca(CH<sub>3</sub>COO)·H<sub>2</sub>O
  - $\rightarrow$  calcium acetate chloride hydrate Ca(CH<sub>3</sub>COO)Cl·H<sub>2</sub>O (calclacite)
  - $\rightarrow$  calcium acetate chloride nitrate hydrate Ca(CH<sub>3</sub>COO)Cl(NO<sub>3</sub>)·H<sub>2</sub>O (thecotrichite)
- Calcium carbonate  $CaCO_3$  + acetic acid  $CH_3COOH$  + formic acid (HCOOH)  $\rightarrow$  calcium acetate formate hydrate Ca(CH\_2COO)(HCOO)·H\_3O<sup>2</sup>
  - (present in Byne's Efflorescence)

Glass and Enamels:

Soda Glass + acetic acid (CH<sub>3</sub>COO)  $\rightarrow$  sodium acetate trihydrate Na(CH<sub>3</sub>COO)·3H<sub>2</sub>O Soda Glass + formic acid HCOOH  $\rightarrow$  sodium formate Na(HCOO)

<sup>1</sup> Formaldehyde can be a source of formic acid (Raychaudhuri and Brimblecombe 2000).

<sup>2</sup> Calcium formate has not been detected alone on calcareous materials; only mixed acetate formate salts have been detected.

GCI surveys of organic carbonyl pollutants (aldehydes and organic acids) in museums in the United States and Europe. The U.S. surveys sampled general locations, such as galleries, storage rooms, and display cases, and obtained inconsistent data: one location had high concentrations of acetic acid, formic acid, and formaldehyde, while another had high levels of formaldehyde and moderate to low organic acid concentrations. The European surveys sampled areas where artifact damage had already occurred. In general, these areas had higher concentrations of the organic acids than were found in locations sampled in the United States. These findings raise many questions, for example: Were low concentrations of formic acid detected because it is a reactive gas and is removed by corrosion of the object? Is acetaldehyde usually present in smaller concentrations than the other pollutants because it is converted into acetic acid, or is less acetaldehyde emitted in the first place?

The photo essays that follow illustrate the kinds of damage that can occur to metals (leaded bronzes, lead objects, stained-glass leads) and calcareous materials (shells, low-fire ceramics such as terra cotta, tiles, and limestones), as well as to artists' colorants.

#### Figure 2.2.

Leaded Bronzes. A spattering of a blue corrosion product, sodium copper acetate carbonate, can be seen on these two leaded bronze objects. Leaded bronzes may exhibit a white acetate corrosion product as well. Photos by Davina Graham. Courtesy of Glasgow City Council (Museums), The Burrell Collection







#### Figure 2.3.

Lead Objects. Lead objects are notoriously susceptible to damage when stored in wood or wood-composite cabinets that offgas organic carbonyl pollutants. The miniature lead statue of a warrior (a) has been severely damaged by acetic acid. The lead figures at right are in a diorama depicting a battle. Emissions, most likely from the display's support board, have corroded the soldiers (b) to such an extent that several have fallen over. The cannon (c) is in a grave state of disrepair. Photos: Jean Tétreault (fig. 2.3a); Barry Knight © English Heritage (figs. 2.3b, 2.3c)





Stained Glass. Stained-glass panels may appear to be in good condition, but investigation of the lead joins may reveal corrosion, caused by the action of organic carbonyl pollutants. Note here that the solder, which contains tin, is not corroded (figs. 2.4b, 2.4c). This is evidence that alloys can be less susceptible to attack by gaseous pollutants. Photos by Davina Graham. Courtesy of Glasgow City Council (Museums), The Burrell Collection









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#### Figure 2.5.

Shells. Byne's Disease, or Byne's Efflorescence, results when organic carbonyl pollutants attack shells. This typically occurs when the shells are stored in poorquality wooden containers, as seen in the mollusk shell stored in a wooden cabinet (a). The characteristic bumps of Byne's Disease (b, c) consist of needle-like crystals (d). The corrosion product takes advantage of flaws in the shell's protective protein layer (e), which eventually is destroyed as the efflorescence grows. Not all shells in the same microenvironment are affected; see (a). Though the damage may seem random, it is a function of the type of shell as well as its age, treatment, and storage. Photos: Cecily M. Grzywacz (fig 2.5a); Tom Moon Photography (figs. 2.5b, 2.5c); Eric Doehne (figs. 2.5d, 2.5e). © J. Paul Getty Trust









(b)

#### Figure 2.6.

Low-Fire Ceramics. This sixth-century B.C. terra-cotta vase (a) (height 123 mm) with red circular decoration has sprouts of calclacite over its surface. SEM images illustrate the two types of white efflorescence: the long splintered efflorescence occurs inside the vase (b); and globular efflorescence is observed on the neck (c). Photos: Lieve Halsberghe









#### Figure 2.7.

Calcareous Materials. Thecotrichite, calcium acetate chloride nitrate hydrate, has been identified on calcareous materials including limestone and certain low-fire ceramics such as tiles and plates. The twentieth-century Egyptian replica carved limestone (a) has been set aside as a study object. Figure (b) illustrates the invasiveness of this organic carbonyl pollutant corrosion. In the images of the plate (c) and the tile (d), one can see how the efflorescence pushes off the decorative glazed layer, destroying the object's aesthetic and cultural value. Photos: Davina Graham/ Courtesy of Glasgow City Council (Museums), The Burrell Collection (figs. 2.7a, 2.7b); Lieve Halsberghe (fig. 2.7c); Dusan Stulik © J. Paul Getty Trust (fig. 2.7d)





#### Figure 2.8.

Organic Colorants. Ozone is a strong oxidizer and causes significant damage to many materials. One of the most obvious changes is alteration of organic colorants. The Japanese print on the right (a) has been exposed to ozone. When it is compared to the unexposed duplicate print on the left, the differences in the colors become apparent. In another experiment (b), a series of artists' pigments were exposed (top), resulting in dramatic changes when compared to the control (bottom). Photos: James R. Druzik © J. Paul Getty Trust





#### Chapter 3 Introduction to Passive Sampling

#### Air Quality Monitoring in Museums

There are currently two general approaches to air quality monitoring: active and passive. In both approaches, pollutants are trapped on an absorbent or a reactive surface and then their concentrations are determined either directly or by means of laboratory analysis.

An active monitoring system uses a pump to pull air into the device, an approach referred to as pumped sampling. With a passive sampling device (PSD), air naturally diffuses into the trap; this is sometimes referred to as diffusive or diffusional sampling. Active monitoring typically requires costly, sophisticated instrumentation and technical expertise. In contrast, passive monitoring is generally less expensive and easier to use. Active sampling, however, remains the primary method for determining the concentration of gases in air against which other methods are validated (Winberry et al. 1999).

Initially, active sampling methodologies were more precise and accurate than passive sampling techniques. However, since the 1970s, significant advances have been made in passive sampling technology and analytical procedures, especially with respect to inorganic pollutants and to aldehydes such as formaldehyde. These improvements resulted from efforts by such U.S. organizations as OSHA, the EPA, and the National Institute of Occupational Safety and Health (NIOSH) to decrease allowable exposure levels for workers (Chan and Rogers 1999; Hanson 1987). Consequently, the differences in accuracy and precision between active and passive sampling substantially decreased. This led to the investigation of passive sampling techniques for conservation use starting in the 1990s (Grzywacz 1993; Grzywacz and Stulik 1992).

Not all compounds regulated for personal exposures pose a risk to collections. For example, carbon monoxide and carbon dioxide pose a threat to human health but not to collections. In fact,  $CO_2$  is used as a fumigant for collections. Likewise, benzene is a human carcinogen, but it poses no known risks to collections. Therefore, it should not be assumed that because OSHA regulates a compound, it should be included in a museum air quality survey. Furthermore, a level considered safe for people is higher than reasonable levels for preservation standards. Limits typically required for human safety are in the parts per million range (Kennedy et al. 1996), whereas damage to artifacts has been correlated

with concentrations in the parts per billion range (Brimblecombe 1999; Cass, Nazaroff, and Druzik 1991; Grzywacz 1989; Grzywacz and Tennent 1996, 1997; Lee, Holland, and Falla 1996; Livingston 1981; Paterakis 1999). In some cases, such as silver damage or tarnishing by hydrogen sulfide, the range can be as low as parts per trillion (Watts 1997).

#### **Passive Sampling**

Today, monitoring the indoor air quality of museums with a passive sampling device is considered an acceptable approach. Passive sampling has many advantages over active sampling for museum monitoring, including selective identification of pollutants, moderate cost, and ease of use. Passive sampling is less disruptive to the ambient environment because it does not require noisy pumps, and the devices can be deployed and retrieved when the museum is closed to visitors. A possible disadvantage is that long exposure times are usually required, from hours to days to weeks, depending on the device (active sampling can be conducted in minutes or hours).

#### **Passive Sampling Devices**

Commercial passive sampling devices suitable for museum use are commonly available to monitor for ozone, nitrogen dioxide, sulfur dioxide, VOCs, and formaldehyde. Although there are no commercially available PSDs to monitor for low concentrations of acetic acid, formic acid, and hydrogen sulfide, PSDs have been developed by university laboratories for these pollutants (Gibson et al. 1997a, 1997b; Shooter, Watts, and Hayes 1995). Also, Gibson and Brokerhof (2001) have developed a PSD for formaldehyde.

A PSD can be as simple as a reactive metal coupon that tarnishes or a paper strip impregnated with a chemical that turns color proportional to concentration similar to pH indicator paper. Because such devices quickly produce visible results that the user can interpret, they are known as direct-reading PSDs. Typically, though, a PSD is a more structured device consisting of a small housing that encloses an active surface or trap behind a diffusion barrier, and it needs to be sent to a laboratory for analysis.

The schematic in figure 3.1 shows the internal arrangement of the typical PSD. The relative alignment and composition of each component can be varied, allowing researchers and manufacturers to design PSDs for specific pollutants at specific concentration ranges. These variables also distinguish the different classes of passive samplers.

#### How does a PSD trap gas molecules?

Diffusion is the mechanism that allows gaseous pollutants to travel to the active surface of a PSD, where they are trapped. Because air flow into a passive sampler is not assisted by a pump, the rate of air sampling with PSDs is as much as three orders of magnitude slower than with active sampling—milliliters per minute compared to liters per minute. This



#### Figure 3.1.

Cross section of a generic passive sampler showing basic elements in the housing: active surface (S), diffusion barrier (B), and diffusion path length (L), the distance between S and B. Drawing by Cecily M. Grzywacz

#### Introduction to Passive Sampling

slower rate can be an advantage or a disadvantage, as discussed below. Because diffusion depends on temperature, this is an important parameter to note when conducting air quality monitoring so that the results can be interpreted correctly.

#### What does the diffusion barrier do?

The diffusion barrier physically limits and controls the diffusion rate of the gaseous air molecules entering the sampler and hence the rates at which pollutants are trapped on the active surface. The barrier can be physical, such as a screen or a membrane, or it can be a static layer of air. Controlling the rate at which the molecules are trapped on the active surface makes it possible to adjust the sensitivity of the device per unit time. The faster the rate, the greater the amount of pollutant that can be detected for a specific period.

The diffusion rate is pollutant-specific and is a function of the distance between the barrier (B) and the active surface (S) (known as the diffusion path length [L]), as well as the area of the active surface. Modifying either feature adjusts the PSD's sensitivity and accounts for the size difference and the variations in exposure time for commercial devices.

Faster sampling rates mean that the device can be exposed for less time to detect the same amount of gas. This is especially advantageous in situations that require short exposure times, for example, in areas that can be monitored only when the museum is closed to the public. A short exposure time is suitable for open areas, such as galleries. A decreased sampling rate increases the exposure time required to detect the same concentration of pollutant. Longer exposure is advantageous for closed environments, such as a case or a cabinet, because it provides more time for equilibrium or constant concentration to reestablish after the enclosure is momentarily opened for placement of a sampling device. Opening the enclosure allows room air, usually less polluted, to enter and dilute the concentration of the pollutant in question.

#### How are pollutants trapped?

The characteristics of the active surface control which pollutant is trapped and how it is ultimately detected. Frequently the active surface contains a reagent that absorbs the pollutant(s) of interest. Some surfaces react chemically with the pollutant to form a new compound that is measured and used to determine the concentration of the original pollutant. PSDs can be manipulated to detect specific pollutants by modifying the chemistry of the active surface. For example, 2,4-dinitrophenylhydrazine is a highly specific chemical used to trap aldehydes. An active surface of potassium hydroxide, a more general chemical, is used to trap and detect acidic gases such as acetic acid and formic acid. Activated charcoal is a nonspecific trap for VOCs that works solely on the basis of physical adsorption.

#### How are results obtained with a PSD?

PSDs that require laboratory analysis are capable of detecting specific pollutants at the ppb range, but this corresponds with an increase in cost and
complexity. Direct-reading PSDs are usually less expensive, but their detection limits are higher, usually in the ppm range. Although their range can be too high for certain museum applications, direct-reading PSDs are appropriate as prescreening tools to determine if an area has a high pollutant concentration that needs further monitoring. These devices usually detect classes of pollutants, for example, acidic gases, rather than a specific pollutant.

#### How is a pollutant's concentration determined with a PSD?

Concentration, as measured by a PSD, is a time-weighted average (TWA; see sidebar). It is a function of the amount of pollutant measured, the sampling rate, and the exposure time.

For the simplest direct-reading devices, such as chemically treated paper strips, concentration is determined by exposing the PSD for the recommended amount of time and comparing the resulting color change to a supplied chart that relates color to concentration. Some direct-reading devices, such as colorimetric diffusion tubes, incorporate the amount of pollutant and the sampling rate into the readings, producing concentrations based on elapsed time, for example, 25 ppm·hr. If the device is exposed for a longer or shorter period than recommended by the manufacturer, the correct pollutant concentration can be calculated simply by dividing the reading by the actual exposure time.

For laboratory-analyzed PSDs, the analyst calculates the concentration by (1) determining the total amount of pollutant trapped by the device's active surface; (2) calculating the volume of air sampled by multiplying the device's sampling rate, supplied by the manufacturer, by the user-supplied exposure time; and (3) dividing the total amount of trapped pollutant by the volume of sampled air.

#### In what units are pollutant concentrations reported for PSDs?

Most direct-reading PSDs give concentrations in ppm or ppb. However, as noted above, results from direct-reading colorimetric diffusion tubes incorporate exposure time, and these readings are reported in the units ppm·hr or ppb·hr, from which concentration is calculated by dividing by the number of hours exposed.

There is no standard for reporting results from laboratoryanalyzed PSDs. Readings can be volumetric measurements (ppm or ppb)<sup>1</sup> or gravimetric measurements ( $mg \cdot m^{-3}$  or  $\mu g \cdot m^{-3}$ ). Volumetric units are temperature and pressure dependent, whereas gravimetric units are not. It is frequently possible to obtain results in both units on request. In general, U.S. manufacturers and laboratories favor ppb or ppm units, and European Union countries report in  $mg \cdot m^{-3}$  or  $\mu g \cdot m^{-3}$ . For convenience, volumetric units are used in this book.

Concentration units are an important consideration as more than one type of PSD may be used to measure air quality in a museum, producing results in two different units (e.g., ppb and  $\mu g \cdot m^{-3}$ ). To compare these readings directly, the results must be in equivalent units. Table 3.1 provides conversion factors to simplify converting between units of ppb and  $\mu g \cdot m^{-3}$  (or ppm and  $m g \cdot m^{-3}$ ) for ten common gaseous pollutants

## **Time-Weighted Average**

In general, all PSD readings and other air quality data are reported as a TWA concentration over the exposure period. Thus these readings are comparable to average temperature and relative humidity. As with any average measurement or reading, a concentration spike is not distinguished, nor are cyclic fluctuations. A reading of 55 ppb for the gaseous pollutant ozone, for example, does not mean that the concentration of this contaminant never spiked above or dipped below this amount during the exposure.

Figure 3.2 illustrates TWA calculations for the same set of data but different intervals.



#### Figure 3.2.

Daily (a), weekly (b), and monthly, quarterly, and semiannual (c) TWA calculations of hourly nitrogen dioxide data collected by the South Coast Air Quality Management District between August 1, 1996, and February 5, 1997.

Pollutant (Gas)	Molecular Weight	X: To convert µg·m <sup>-3</sup> to ppb or mg·m <sup>-3</sup> to ppm, multiply by	Y: To convert ppb to μg∙m <sup>−3</sup> or ppm to mg∙m <sup>−3</sup> , multiply by
Acetaldehyde, CH <sub>3</sub> CHO	44.05	0.55	1.83
Acetic acid, CH <sub>3</sub> COOH	60.05	0.40	2.49
Ammonia, NH <sub>3</sub>	17.03	1.42	0.71
Carbonyl sulfide, CO	60.08	0.40	2.49
Formaldehyde, HCHO	30.03	0.80	1.25
Formic acid, HCOOH	46.03	0.52	1.91
Hydrogen sulfide, H <sub>2</sub> S	34.08	0.71	1.41
Nitrogen dioxide, NO <sub>2</sub>	46.01	0.52	1.91
Nitrogen monoxide, NO	30.01	0.80	1.25
Ozone, O <sub>3</sub>	48.00	0.50	1.99
Sulfur dioxide, SO <sub>2</sub>	64.07	0.38	2.66
Total VOCs as n-hexane	86.17	0.28	3.57

#### Table 3.1.

Concentration conversion factors for common gaseous pollutants. This table provides conversion factors between  $\mu g \cdot m^{-3}$ and ppb (or mg·m<sup>-3</sup> and ppm), and vice versa, at standard temperature and pressure (STP) as defined by the Compressed Air and Gas Institute; T = 20°C, P = 1 atmosphere. To use the table to convert a concentration reported in  $\mu g \cdot m^{-3}$  (or mg·m<sup>-3</sup>) to one in ppb (or ppm), multiply the concentration by the corresponding number for that gas in column X. Multiply the ppb concentration by the number in column Y to convert it to  $\mu g \cdot m^{-3}$ . found in museum environments.<sup>2</sup> An online concentration converter is also available.<sup>3</sup>

## Selecting the Appropriate PSD

Selecting the appropriate PSD to monitor air quality in museum environments requires an understanding of such factors as their detection limits, precision and reproducibility, accuracy, specificity and interferences, and exposure times. These parameters, which are frequently reported in the manufacturer's literature, are reviewed here. Also covered is PSD sensitivity to light, temperature, and storage time.

#### **Detection limit**

The detection limit of a device is an important parameter to consider when deciding on a PSD. Not all monitors available for air quality testing, especially those developed for laboratory safety and industrial hygiene, have detection limits appropriate for museum environmental studies. For example, the detection limit may be too high; that is, the sampler does not detect gaseous pollutants at the low ppb concentrations considered a potential risk to collections.

Selecting a PSD with detection limits too high relative to the pollutant concentrations in the museum environment being tested can report a false negative. This could be a critical error if sensitive materials are placed in an environment that was tested and reported as not having the potentially damaging gas present. Because a PSD does not detect a pollutant does not mean it is not present. It can only be stated that the pollutant is present at concentrations less than the detection limit of the device. (See Appendix 2 for target pollutant guidelines that aid in evaluating the suitability of the detection limits of the PSD being considered for a monitoring program.)

#### Sampler precision and reproducibility

A PSD's precision is measured by the reproducibility of its readings. Ideally, the readings from a set of colocated PSDs should be identical. This is not always the case, however, and using multiple samplers will improve precision by averaging the concentrations detected. Based on the reproducibility of a device for a particular gas, the manufacturer will recommend how many devices should be used in each area of interest.

Reproducibility is a function of the design of the device, the analysis method, and, in the case of laboratory-analyzed PSDs, the laboratory's compliance with the analysis method or protocol. Most commercially available devices have good reproducibility, and exposure of one device per location is satisfactory (Grzywacz and Villalta 1998, 1999). However, reproducibility problems have been reported with noncommercial PSDs prepared and analyzed in a laboratory not familiar with the procedure (Brokerhof, Gibson, and Grzywacz 1998).

## Accuracy

A PSD's accuracy is defined by how close its reading is to the true value. Figure 3.3 illustrates the difference between precision and accuracy. The device's manufacturer or inventor determines accuracy by exposing the PSD to a known concentration of pollutant and comparing the results with those obtained by a primary method of analysis, such as active sampling.

#### Specificity and interferences

The composition of air, especially indoor air, is complex. Analysis of air in most rooms will reveal the presence of hundreds of chemical species, the majority of which are not damaging to collections. If the active surface in a PSD can trap more than one gas, then it is not specific, and some of these other contaminants will be collected as well. This is known as interference. Interference is usually not a problem for most PSDs that require laboratory analysis. If the trapping reagent is not specific, the devices merely trap the gases, and the laboratory uses chromatography, a separation technique, to determine the concentration of the specific gases of interest.

On the other hand, many direct-reading PSDs are nonspecific and especially subject to interference from other gases. The reagent in their active surface is sensitive to classes of compounds, producing a color change that is proportional to the total concentration of gases, not just the target pollutant. For example, a direct-reading diffusion tube PSD for acetaldehyde will react with all aldehydes present in the environment. Even though a PSD is not specific—that is, it is subject to interferences—a positive result still provides important information about a possible problem that would warrant additional testing with more specific PSDs.

#### **Exposure time**

Because PSDs record concentrations as a time-weighted average, extending exposure time improves the detection limit of the device. By deploying a sampler longer, the pollutant has more time to react with the active surface of the sampler and to be trapped, which increases the detection limit. When attempting to detect extremely low pollutant concentrations, it is necessary to lengthen exposure times. In most situations, the exposure time should be as long as possible within the restrictions of the PSD.

However, one trade-off in increasing the exposure time may be degradation of the chemical reagents used by the PSD to trap airborne pollutants, as well as the reaction products. Some samplers can be safely



## Figure 3.3.

Precision versus accuracy: (a) poor precision and poor accuracy; (b) precision high but accuracy poor (all the arrows are in the same region); (c) high precision and high accuracy (all arrows hit the bull's eye). Drawing by Cecily M. Grzywacz

exposed for up to thirty days; others may start to fade and produce erroneous results after only eight hours. The PSD's manufacturer or vendor should be consulted when extending the exposure time beyond the recommended limit.

## Light, temperature, and storage time sensitivity

Reagents and reaction products on the active surface can also be sensitive to degradation by light, especially UV light, and temperature. A few are even unstable with respect to storage time. These sensitivities reduce the sampler's capacity and results in erroneously low readings of pollutant concentrations. Because of temperature sensitivity, manufacturers often recommend storing susceptible samplers in freezers or refrigerators before and after exposure. To minimize degradation from sunlight, the PSDs can be placed under an opaque shelter when used outdoors (Smith et al. 2000). This could be the same shelter used to minimize air velocity effects (see sidebar "Considerations in the Use of Open-Path (Palmes) Diffusion Tubes," chap. 4). Some manufacturers will specify shelter requirements for their devices. Finally, attention to expiration dates will avoid degradation from prolonged storage, but not all vendors provide them.

## Conclusion

The increasing accuracy, precision, and low limits of detection of passive sampling devices, along with ease of use, low technical knowledge required, and economy, make them ideal for air quality monitoring studies in museums. Chapter 4 discusses in detail the various types of PSDs that are available commercially and from private laboratories.

#### Notes

- 1. A few commercially available devices also indicate a volumetric concentration as ppbv.
- 2. To obtain an approximate conversion between ppb and µg·m<sup>-3</sup>, or ppm and mg·m<sup>-3</sup>, some people use a "one-half rule": a ppb (or ppm) value is roughly equivalent to one-half the µg·m<sup>-3</sup> (or mg·m<sup>-3</sup>) value. However, this relationship is a mathematical coincidence only for ozone and should not be used.
- 3. The handy online concentration converter for gaseous pollutants (http://iaq.dk/ papers/conc\_calc.htm) converts concentration units of µg·m<sup>-3</sup> to ppb and mg·m<sup>-3</sup> to ppm. The concentration converter accounts for the volume change of a gas with temperature and pressure. The user is asked to supply the temperature and pressure during the monitoring. However, for ease of comparison, it is recommended to use standard temperature and pressure (STP) as defined by the Compressed Air and Gas Institute (www.cagi.org): 20°C (68°F) and 1013 hPa (1 atmosphere or 760 mm Hg). The last item required by the converter is the molecular weight of the pollutant being measured, which is provided in a table for a number of important gases found in museum environments.

## Chapter 4 Passive Sampling Devices

Many different types of passive sampling devices are available to detect gaseous pollutants found inside museums. This chapter discusses the classification of PSDs, describes what distinguishes one from the other, and then introduces specific monitors that are commercially available to the museum community.

## Classification

PSDs are classified generally as either direct reading or laboratory analyzed. Results from a direct-reading device are immediately available after an exposure of minutes or hours. A few PSDs require an exposure of days or weeks before they can be read. Direct-reading devices are based on the reaction between the chemical(s) on the PSD's active surface and the gases present in the air, usually resulting in a color change. Although they provide almost instantaneous results, they are not always as informative as laboratory-analyzed devices, whose results typically are not received for one to three weeks after exposure. The advantages of the laboratoryanalyzed PSD, however, are greater accuracy, precision, and specificity.

Both direct-reading and laboratory-analyzed PSDs can be either qualitative or quantitative. Data from qualitative PSDs can be used to indicate potential risk to collections from indoor air quality. In contrast, quantitative devices provide actual pollutant concentrations, reported as a volumetric (ppm or ppb) or gravimetric measurement (mg·m<sup>-3</sup> or  $\mu$ g·m<sup>-3</sup>).

Table 4.1 is an alphabetic listing of PSDs that indicates which pollutants can be detected with which type of device. It can be used as a key to the detailed information presented in tables 4.2 through 4.5. For example, if you are interested in a sampler to detect formaldehyde, go to the column in table 4.1 for formaldehyde and read down to locate the available samplers; if you want to know which pollutants can be detected with a particular device, find the row in table 4.1 and read across. Next, check the appropriate table noted in column 1 of table 4.1 for detailed information on vendor, cost, sensitivity, and so on.

Tables 4.2 through 4.5 amplify the discussion of the variety of PSDs applicable to museum monitoring presented in this chapter. They are comprehensive, though not exhaustive, illustrated inventories of com-

Passive Sampling		Acetic	Formic	Formal-	Acetal-	Total			NO/		
Device	Table	Acid	Acid	dehyde	dehyde	VOCs <sup>a</sup>	Η₂S <sup>b</sup>	NO2	NOx⁰	Ozone	50 <sub>2</sub>
A-D Strips	4.2	Yes	Yes				p	_	_		_
AirScan <sup>®</sup> 1056 Low Level Formaldehyde Monitor	4.3			Yes							
Bio-Check Badges	4.3			Yes						Yes	
ChemDisk <sup>TM</sup> Personal Monitors	4.5	Yes	Yes	Yes	Yes	Yes				Yes	
ChromAir <sup>TM</sup> Colorimetric Badges	4.3			Yes				Yes		Yes	Yes
Dräger Color Diffusion Tubes	4.3	Yes	Yes					Yes			Yes
EcoBadge®	4.3									Yes	
Environmental Reactivity Coupons – Purafil®	4.4	Yes	Yes				Yes	Yes			Yes
GMD Formaldehyde Dosimeter Badge	4.5			Yes	Yes <sup>e</sup>						
Gastec <sup>TM</sup> Color Dosimeter Tubes	4.3	Yes	Yes	Yes	Yes			Yes			Yes
Gradko Diffusion Tubes	4.5			Yes		Yes	Yes	Yes	Yes	Yes	Yes
IVL Diffusive Sampler	4.5	Yes	Yes					Yes	Yes	Yes	Yes
Kem Medical Vapor-Trak® Badges	4.5			Yes							
Leak-Tec® badges	4.3							Yes			
Metal coupons	4.2	Yes	Yes	Yes			Yes	Yes	Yes		Yes
Ogawa Passive Sampler	4.5							Yes	Yes	Yes	Yes
Oxford Brookes University Open-Path Diffusion Tube	4.5	Yes	Yes				Yes	Yes		Yes	Yes
Ozone Test Sticks	4.3									Yes	
SafeAir <sup>TM</sup> Colorimetric Badges	4.3			Yes				Yes		Yes	Yes
SKC 526 Formaldehyde Passive Sampler for Indoor Air Sampling	4.5			Yes							
SKC 575 Passive Sampler for Organic Vapors	4.5					Yes					
SKC Formaldehyde Passive Sampler for Personal Sampling	4.5			Yes							
3M <sup>TM</sup> Air Monitors	4.5			Yes		Yes					
UMEx 100 <sup>TM</sup> Passive Sampler for Formaldehyde	4.5			Yes	Yes						
University of Strathclyde Museum Diffusion Tubes	4.5	Yes	Yes	Yes							
<sup>a</sup> Total VOCs are usually reported as n-hexane. Some laboratories also quantify one to th <sup>b</sup> Only devices that can measure in the ppt range or low ppb concentrations are indicated <sup>c</sup> NOx is the sum of NO and NO <sub>2</sub> . <sup>d</sup> I = interference. The acidic form of these pollutants are detected, e.g., $H_2SO_4$ , $HSO_3$ , are <sup>c</sup> saminir france for the form of these Annondix 4. 1 hile A4.1	iree specific ch d here. Severa nd HNO <sub>3</sub> .	nemicals. Base I of these mar	d on the mate nufacturers ha	erials and acti ve samplers t	vities in the al hat detect pp	rea to be sam m H <sub>2</sub> S, but th	pled, these c is is not ade	hemicals can quate for mus	be requested seum monitor	ing.	
Jamphills Late 101 accurations is required, see appendix 7, were seen											

 Table 4.1.
 Selected passive sampling devices by pollutants

#### Passive Sampling Devices

mercially available PSDs (and a few offered by universities) that include device specifications and vendor contact information. New products are constantly being developed and made available and old products improved; it is recommended that you check regularly with specific vendors such as Lab Safety Supply, Inc., and SKC, Inc., and visit specific conservation websites, such as the Indoor Air Quality Working Group (see chap. 1, sidebar "Useful Websites"). Those devices that were used by the GCI are so noted in the tables. However, this is neither an endorsement nor a recommendation of these products. Furthermore, several of the PSDs discussed in this chapter are new to the conservation community. The selection of samplers presented here is based on the criteria presented in chapter 3: detection limit, precision, reproducibility, accuracy, specificity, interferences, exposure time, and sensitivity to environmental conditions. When selecting an air quality monitor, the two major opposing factors are cost and sensitivity.

## **Direct-reading PSDs**

#### Qualitative direct-reading PSDs

Qualitative direct-reading PSDs (see table 4.2) do not rely on controlled diffusion as do other more sophisticated devices and thus have no diffusion barrier. These PSDs are simply an active surface, which is usually nonspecific, that reacts with pollutants in the environment. With appropriate cautions that are discussed in chapter 5, qualitative direct-reading PSDs are a practical way to monitor changes in environmental conditions, especially over the long term. They are also useful as prescreening tools to identify an area with a high pollutant concentration that needs further monitoring. This screening capability maximizes the use of more sophisticated and costlier PSDs. Qualitative direct-reading PSDs are coupons of at-risk materials or chemically treated test strips.

Test strips. Dye-coated test strips, like universal pH-indicating paper, change colors in response to the environment. A commercially available qualitative test strip is

#### • A-D Strips — acetic acid and other acid gases

**Coupons.** These standardized pieces of a test material are simple PSDs, yet they are useful indicators of environmental quality. Coupons are most commonly metals, but almost any other material representative of the collection at risk can be used, for example, paper, shell, glass, or limestone.

*Metal coupons.* Metal coupons are a simple way to determine a corrosive environment. These samplers are small squares of the same metals found in the at-risk collection. Metal coupons, which may be mounted on a support, can be discretely placed in a microenvironment, for example, in a display case, and observed for changes that indicate a potentially damaging condition. Either the surface dulls or the material corrodes compared to a control (an unexposed and protected coupon). The lead coupon in figure 4.1 is covered with a white powder, most likely basic lead carbonate (lead white), after being exposed in a storage cabi-

## Table 4.2.

Selective qualitative direct-reading PSDs for monitoring museum environments

Sampling Device		Manufacturer's Information	Supplier(s)
A-D Strips	Courtesy of the Image Permanence Institute of the Rochester Institute for Technology	<ul> <li>Pollutant(s) detected: Acetic acid and other acidic gases</li> <li>Exposure time: 24 hours to 6 weeks</li> <li>Concentration range: Estimated to be 1–45 ppm</li> <li>Cost (2004): \$45 for package of 250 strips; includes color reference pencil</li> <li>Interferences: Any other acidic species</li> <li>Caution: Reactive surface is light sensitive, which is important for long-term</li> </ul>	Image Permanence Institute www.rit.edu/~661www1/sub_pages/ 8contents.htm Rochester Institute of Technology 70 Lomb Memorial Dr. Rochester, NY 14623-5604 Tel: 585-475-5199
oped A-D Strips specifically to detect acetic acid released from decomposing cellulose acetate films, such as those in collections of cinema film, microfilm, or pictorial film. Independent testing, how- ever, confirmed that these strips are quick and economical passive sampling devices for conservation purposes (Nicholson and O'Loughlin 1999).		exposures in lighted areas. Analysis: Compare color of exposed strip to color reference pencil.	
These strips were used to mounts in newly construc walls for leaded glass pan Getty Museum at the Get	evaluate ted freestanding els at the J. Paul tty Center.		
GCI Guest Scholar A. Pate A-D Strips in her Bronze ( Project (Paterakis 2004).	erakis used the Corrosion		
Metal Coupons		Pollutant(s) detected: Chlorides; reduced	For copper, lead, and silver:
	Photo: David Carson © J. Paul Getty Trust	sulfides; inorganic acids, such as sec- ondary pollutants from NO <sub>2</sub> and SO <sub>2</sub> ; organic carbonyl pollutants	Alfa Aesar www.alfa.com 26 Parkridge Rd.
1 cm		Exposure time: Weeks to months	Ward Hill, MA 01835 Tel: 978-521-6300
1 inch Metals for coupons are suppl form of sheets, foils, and tap sometimes can be ordered pr	pplied in the tapes, and   precut to size.	ppb and greater for other metals <b>Cost (2004):</b> per 1 cm square of a 1.0 mm foil 99+%: \$5 copper, Cu \$5 lead, Pb (see health caution <sup>a</sup> ) \$25 Silver, Ag	Goodfellow Corporation www.gwww.goodfellow.com 237 Lancaster Ave., Ste 252 Devon, PA 19333-1954 Tel: 610-688-4262 Toll-free: 800-821-2870
		Interferences: Not applicable; this is a nonspecific test for corrosivity.	National Bronze & Metals Inc. www.nbm-houston.com
		<b>Caution:</b> Do not use polishing products that have anti-tarnish addtitives.	Houston, TX 77008 Tel: 713-869-9600
		<b>Analysis:</b> Visual and microscopic compar- ison with control coupon.	Toll-free: 800-231-0771 Sigma-Aldrich
		Buehler Ltd. provides polishing supplies: www.buehler.com 41 Waukegan Rd. Lake Bluff, IL 60044 Tel: 847-295-6500 Toll-free: 800-BUEHLER (1-800-283-4537)	www.sigmaaldrich.com 3050 Spruce St. St. Louis, MO 63103 Toll-free: 800-521-8956
<sup>a</sup> Caution Health Hazard, NFPA ra for guidelines.	ting 4 of 4 and a carcinogen.	Personnel protection equipment should always be worn when h	andling metallic lead. See Stravroudis 1997a, 1997b



net. Using metal coupons for passive sampling is a variation of the British Standard Test or Oddy test,<sup>1</sup> but it is performed under ambient conditions (Oddy 1973).

Metal coupons allow general deductions regarding the pollutants present in an environment. Different metals react to specific kinds of pollutants. Copper corrosion is often associated with chlorides, sulfides, and acidic pollutants such as  $NO_2$  and  $SO_2$ . Silver reacts with sulfides such as carbonyl sulfide (COS) and hydrogen sulfide (H<sub>2</sub>S). Lead reacts with organic carbonyl pollutants and other acid pollutants. The relative rate of corrosion of a metal coupon—fast, moderate, or slow—can be used to indicate the severity of the air quality problem. If desired, the exposed metal coupons or surface scrapings can be analyzed to determine the composition of the corrosion product, but this is usually expensive and not necessary for general air quality monitoring (see table 4.4 for a description of metal coupons designed specifically for laboratory analysis).

Although not specifically marketed for air quality monitoring, high-quality or certified metal sheets, tapes, and foils of copper, lead,<sup>2</sup> and silver are available commercially and can be used as metal coupons. They can be purchased precut, or they can be cut by the user into a standard size, such as 1 cm<sup>2</sup>, 2.5 cm<sup>2</sup>, or a rectangle 1 to 2 cm long. Prior to use, the tarnish or oxide layer on the metal coupons needs to be removed in order to expose a fresh surface that is more reactive than the metal of the objects. This step should be approached cautiously, because polishing pastes may contain chemicals, such as oils and corrosion inhibitors, that prevent the metal coupon from reacting with the corrosive gases in the test environment. Although copper, lead, and silver are the most common coupons, other metals, including alloys such as brass and bronze, can also be used to evaluate environmental risk. It is important to use a metal that most closely represents the at-risk collection and to use the same metal

#### Figure 4.1.

Corrosion on lead coupon exposed in a storage cabinet indicating presence of organic carbonyl pollutants. Photo: Dusan Stulik © J. Paul Getty Trust

quality and coupon size to allow comparison when exposing multiple coupons in different locations or at different times.

Metal sheets, foils, and tapes suitable for museum monitoring are available from the following vendors:

- Alfa Aesar copper, lead, and silver
- Goodfellow Corporation copper, lead, and silver
- National Bronze & Metals, Inc. bronze and copper
- Sigma-Aldrich copper, lead, and silver

Other coupons. Any material representative of a collection can be used as a qualitative direct-reading PSD, for example, various stones for building materials, shells for natural history collections (e.g., Brokerhof and van Bommel 1996), or glass for enamels. Again, the material should be more susceptible to damage than the objects in the collections, so that damage is seen on the coupon before it occurs on the object. Usually, the coupon is prepared by simply cleaning the surface.

In situ metal indicators. Sometimes qualitative monitoring of a microenvironment can be the serendipitous observation of corrosion on metal parts on a collection's housing. Corroded lock mechanisms, screws, hinges, bolts, and so on, are, in a sense, in situ metal coupons that warn of a potential risk from gaseous pollutants. This is why it is important when conducting a museum survey to note alterations of any materials used in a case, cabinet, gallery, and storage room containing a collection, even if the changes seem insignificant at the time or their implications are not fully understood. (See sidebar "Monitoring in Action: Santa Barbara Museum of Art" for an example.)

If a metal component of a cabinet or display case corrodes, this does not necessarily mean that the collection inside is at risk. Interpretation of such incidents is subjective, similar to the interpretation of the results of the Oddy test (Green and Thickett 1993). For example, objects made of porcelain, a high-fire ceramic, that are stored in a cabinet with corroded zinc-plated locks are minimally at risk from the gases that caused the corrosion. However, if the collection consists of works of art on paper that include metal appliqués or foil inlays, then an objectionable risk is likely. In contrast, if wood sculptures are on display and metal parts of the display case indicate the presence of damaging gases, the wood of the sculptures—not gases from the display case—could be the culprit (see chap. 5). Similarly, natural history specimens can be the source of contamination, especially specimens stored in formalin.

Other in situ indicators. Any material that alerts one to a potentially damaging microenvironment can be used as a PSD. Deterioration of paper labels has been observed for years. The labels can be considered an in situ indicator of acidic conditions. Paper squares or "coupons" can be placed in microenvironments as a PSD.

#### Quantitative direct-reading PSDs

In addition to indicating that a certain pollutant is present in the atmosphere, a quantitative direct-reading device determines the amount or concentration of that gas (see table 4.3). Quantification is the result of a color

## Table 4.3

Selected quantitative direct-reading PSDs for monitoring museum environments

Sampling Device	Manufacturer's Information	Supplier(s)
AirScan <sup>®</sup> Badges (AirScan 1056 Low Level Formaldehyde Monitor TWA)	<ul> <li>Pollutant(s) detected: Formaldehyde</li> <li>Exposure time: STEL<sup>a</sup> (15 min) or TWA (8 hr). Can extend exposure up to 24 hours.</li> <li>Concentration range: 5–55 ppb; minimum detectable, 30 ppb in 8 hours</li> <li>Cost (2004): \$50 each or \$272 for pack of 6</li> </ul>	Interferences: Ammonia; acetaldehyde and other aldehydes Analysis: The length of the line that develops is proportional to the concentration of formalde- hyde. The concentration is obtained from the conversion chart supplied with the monitor. Lab Safety Supply, Inc. www.lss.com P.O. Box 1368 Janesville, WI 53547-1368 Toll-free: 800-356-0783 Safe Home Products www.safehomeproducts.com Tel: 319-354-7301 Toll-free: 888-607-9902 <i>Note:</i> AirScan Environmental Technologies, Inc., manufacturer of AirScan Badges, does not sell these devices directly.
Bio-Check-F badge Courtesy of Dräger Safety, Inc.	Pollutant(s) detected: Formaldehyde Exposure time: 2 hours Concentration: 0.05 to 0.3 ppm Cost (2004): ~\$150 Interferences: None; device is enzyme based and specific for formaldehyde. Analysis: Color change from white to pink to red with increasing concentration.	Dräger Safety www.draeger.com Locations in several countries. Dräger Safety, Inc. 101 Technology Dr. Pittsburgh, PA 15275-1057 Tel: 412-787-8383 Dräger Safety UK Ltd. Kitty Brewster Industrial Estate Blyth Northumberland NE24 4RG United Kingdom Tel: +44 1670 35 2891
Bio-Check-Ozone badge Bio-Check Ozon Organowski and Alexandrowski and Alexandrowski and Alexandrowski and Alexandrowski and Alexandromski	Pollutant(s) detected: Ozone Exposure time: 10–20 minutes Concentration: Less than 15 ppb to greater than 105 ppb Cost (2004): \$99 for 10 samplers Interferences: None cited. Analysis: Compare color developed with scale pro- vided by manufacturer.	Dräger Safety www.draeger.com Locations in several countries. Dräger Safety, Inc. 101 Technology Dr. Pittsburgh, PA 15275-1057 Tel: 412-787-8383 Dräger Safety UK Ltd. Kitty Brewster Industrial Estate Blyth Northumberland NE24 4RG United Kingdom Tel: +44 1670 35 2891

Note: <sup>a</sup> STEL is the short-term exposure limit, a 15-minute TWA exposure that should not be exceeded at any time during a workday. It is defined by the National Institute of Occupational Safety and Health (NIOSH; www.cdc.gov/niosh).

## Table 4.3 (continued)

Sampling Device	Manufacturer's Information	Supplier(s)
ChromAir <sup>®</sup> Colorimetric Badges Courtesy of Morphix Technologies Clear, easy-to-read color change. No lab analysis needed or no chemicals to mix. Available with color comparator to increase resolution and concentration range.	<ul> <li>Pollutant(s) detected: Formaldehyde, nitrogen dioxide, ozone, sulfur dioxide</li> <li>Exposure time: <ul> <li>Formaldehyde, NO2, SO2: 15 minutes to 2 days</li> <li>Ozone: 5 minutes to 10 hours</li> </ul> </li> <li>Concentration range: <ul> <li>Formaldehyde: 0.3 to 40 ppm·hr</li> <li>NO2: 0.35 to 40 ppm·hr</li> <li>Ozone: 0.08 to 2.6 ppm·hr</li> <li>SO2: 0.1 to 65 ppm·hr</li> <li>Cost (2004): \$131 per pack of 10</li> </ul> </li> <li>Interferences: <ul> <li>Formaldehyde: acrolein and aldehydes</li> <li>NO2: chlorine, ozone reacts with same sensitivity</li> <li>Ozone: hydrogen peroxide, NO2</li> <li>SO2: none known</li> </ul> </li> <li>Analysis: Compare colors developed in six windows with comparator chart and read concentration in ppm·hr; divide by exposure hours to obtain average concentration.</li> </ul>	K & M Environmental Air Sampling Systems www.kandmenvironmental.com 2557 Production Rd. Virginia Beach, VA 23454 Tel: 757-431-2260 Toll-free: 800-808-2234 Lab Safety Supply, Inc. www.lss.com P.O. Box 1368 Janesville, WI 53547-1368 Toll-free: 800-356-0783
Courtesy of SKC, Inc.	<b>Pollutant(s) detected:</b> Acetic acid, nitrogen dioxide, or sul- fur dioxide	Dräger Safety www.draeger.com Locations in several countries
	<b>Exposure time:</b> 1–24 hours; some can be exposed for days (check with manufacturer)	Dräger Safety, Inc.
	Concentration: Acetic acid: 1.3 to 200 ppm·hr	101 Technology Dr. Pittsburgh, PA 15275-1057
<b>P</b> -0	NO <sub>2</sub> : 1.3 to 200 ppm hr SO <sub>2</sub> : 0.7 to 150 ppm hr	Tel: 412-787-8383 Dräger Safety UK Ltd.
These inexpensive PSDs are a useful	<b>Cost (2004):</b> \$75–\$100 per box of 10	Kitty Brewster Industrial Estate Blyth
screening technique for ruling out high concentrations of pollutants.	<b>Interferences:</b> Diffusion tubes are sensitive to a class of pollutants but not specific gases; e.g., acetic acid diffusion tube is sensitive to all acids, not only acetic acid.	Northumberland NE24 4RG United Kingdom Tel: +44 1670 35 2891
Dräger acetic acid color diffusion tubes were used by GCI Guest Scholar A. Paterakis to track initial concentra-	Analysis: Read length of color development using the printed calibrated scale in ppm·hours and divide by the	Lab Safety Supply, Inc. www.lss.com
tions during a corrosion experiment (Paterakis 2004).	number of hours exposed. Note: These tubes should not be confused with detector	P.O. Box 1368 Janesville, WI 53547-1368
Successfully used at GCI and other	tubes, which Dräger also manufactures. Detector tubes require a pump and are a direct reading, active sampling	Toll-free: 800-356-0783 SKC, Inc.
erate to high levels of organic carbonyl pollutants in display cases and other	method.	www.skcinc.com/passive.asp 863 Valley View Rd. Fighty Four, PA 15330
pollutants in storage rooms.		Tel: 724-941-9701 Toll-free: 800-752-8472 (USA only)
EcoBadge®	Pollutant(s) detected: Ozone	Vistanomics, Inc.
Courtesy of Vistanomics Inc	Exposure time: 1–8 hours	www.ecobadge.com P.O. Box 847
	Concentration range: 20–240 ppb	Montrose, CA 91021-0847 Tel: 818-249-1236
	Interferences: None	VWR International Scientific
	Analysis: Compare color development with a colorimetric	www.vwr.com

GCI has used these badges as a quick short-term screening tool for ozone at various institutions.

**Analysis:** Compare color development with a colorimetric comparison chart provided by the manufacturer. White paper turns pink to purple for 1-hour exposures; tan to brown for 8-hour exposures.

www.vwr.com 1310 Goshen Pkwy West Chester, PA 19380 Toll-free: 800-932-5000

Sampling Device	Manufacturer's Information	Supplier(s)
Gastec <sup>™</sup> Color Dosimeter Tubes Courtesy of SKC, Inc. Similar to Dräger color diffusion tubes described previously. Successfully used at GCI to detect moderate to high levels of organic carbonyl pollutants in display cases as well as other gases in storage rooms. Note: These tubes should not be con- fused with detector tubes, which the Gastec Corp. also manufactures. Detector tubes require a pump and are a direct reading, active sampling method.	Pollutant(s) detected: Acetaldehyde*, acetic acid, formaldehyde, formic acid*, hydrochloric acid*, nitric acid*, $NO_2$ , and $SO_2$ . Exposure time: 15 minutes to 24 hours Concentration: Acetaldehyde: 0.1–20 ppm·hrs Acetic acid: 0.5–100 ppm·hrs Formaldehyde: 0.1–20 ppm·hrs Formic acid: 0.55–110 ppm·hrs Formic acid: 0.55–110 ppm·hrs HCI: 1–100 ppm·hrs HNO <sub>3</sub> : 0.32–32 ppm·hrs NO <sub>2</sub> : 0.01–30 ppm·hrs SO <sub>2</sub> : 0.2–100 ppm·hrs Cost (2004): \$55–\$65 for box of 10 Interferences: See Dräger Diffusion Tubes above. Analysis: Read concentration in ppm·hr at length of color development and divide by exposure time in hours to obtain average concentration. *This is a secondary application for this tube and requires a correction factor. See operating instructions provided by the manufacturer.	Lab Safety Supply, Inc. www.lss.com P.O. Box 1368 Janesville, WI 53547-1368 Toll-free: 800-356-0783 SKC, Inc. www.skcinc.com/passive.asp 863 Valley View Rd. Eighty Four, PA 15330 Tel: 724-941-9701 Toll-free: 800-752-8472 (USA only) <i>Note:</i> Gastec Corp. does not sell these devices directly.
Leak-Tec® badgesImage: Contract of the second	Pollutant(s) detected: Ozone Exposure time: Minutes to hours Concentration range: 0.1 ppm in 15 minutes Cost (2004): \$7 for holder; \$25 for 10 color-change strips Interferences: None noted. Analysis: Color changes from white to brown.	Lab Safety Supply, Inc. www.lss.com P.O. Box 1368 Janesville, WI 53547-1368 Toll-free: 800-356-0783 American Gas & Chemical Co. Ltd. www.amgas.com 22 Pegasus Ave. Northvale, NJ 07647 Tel: 201-767-7300 Toll-free: 800-288-3647
Ozone Test Sticks Courtesy of SKC, Inc.	<ul> <li>Pollutant(s) detected: Ozone</li> <li>Exposure time: 10 minutes</li> <li>Concentration range: 45 to 105 ppb (<i>Note:</i> Although 45 ppb is a high reading, this level could be encountered in naturally ventilated buildings.)</li> <li>Cost (2004): \$62.50 for 50 strips</li> <li>Interferences: Oxidizing reagents such as chlorine.</li> <li>Analysis: Compare color development with scale provided.</li> </ul>	SKC, Inc. www.skcinc.com/passive.asp 863 Valley View Rd. Eighty Four, PA 15330 Tel: 724-941-9701 Toll-free: 800-752-8472 (USA only)
SafeAir <sup>®</sup> Colorimetric Badge Courtesy of Morphix Technologies	<ul> <li>Pollutant(s) detected: Formaldehyde, NO<sub>2</sub>, ozone, and SO<sub>2</sub></li> <li>Exposure time: Formaldehyde: 15 minutes to 16 hours; NO<sub>2</sub>: 15 minutes to 10 hours; Ozone: 15 minutes to 2 days; SO<sub>2</sub>: 15 minutes to 2 days</li> <li>Concentration range: Formaldehyde: 0.05 ppm (8 hr) to 0.4 ppm·hr; NO<sub>2</sub>: 0.125 ppm (8 hr) to 1.0 ppm·hr; Ozone: 0.006 ppm (8 hr) to 0.05 ppm (8 hr) to 0.2 ppm·hr</li> <li>Cost (2004): \$150-\$160 for 50 badges</li> <li>Interferences: Formaldehyde: acrolein and aldehydes; NO<sub>2</sub>: ozone, chlorine; Ozone: hydrogen peroxide, NO<sub>2</sub>; SO<sub>2</sub>: none</li> <li>Analysis: When exposed to pollutant at threshold concentrations, an exclamation point changes color.</li> </ul>	K & M Environmental Air Sampling Systems www.kandmenvironmental .com/ 2557 Production Rd. Virginia Beach, VA 23454 Tel: 757-431-2260 Toll-free: 800-808-2234 Lab Safety Supply, Inc. www.lss.com P.O. Box 1368 Janesville, WI 53547-1368 Toll-free: 800-356-0783

## Monitoring in Action: Santa Barbara Museum of Art

In the mid-1980s the GCI conducted an environmental survey of nearly six hundred locations in seventeen museums (Grzywacz 1989). The Santa Barbara Museum of Art in Santa Barbara, California, was one of the participants. While working with GCI scientists to select locations to represent display cases, storage cabinets, galleries, and storage areas at the museum, the assistant registrar pointed out a recent observation in one of the vault areas. The lock mechanisms on the inside of the storage cabinets were dulling. They were originally bright, shiny locks. On closer inspection, even the screws in the lock plate were dull, and the external cabinet handle was corroded as well (fig. 4.2a, b).

The storage cabinets had been constructed of high-grade marine birch particleboard with a hardwood laminate to house a variety of objects, including Asian objects, small sculptures, and small decorative arts. The cabinets were 6 feet high by 2 feet deep by 5 feet wide with double doors that locked shut (Grzywacz, Taketomo, and Stulik 1988). The GCI scientists learned that the cabinets had been recently modified to improve protection to the objects in the event that an earthquake would occur when the doors were open or would cause the doors to open. To prevent objects from

moving across a shelf and falling to the floor during a tremor, strips of the original laminated particleboard were cut and secured about 3 inches above shelf level (fig. 4.3). The intent of this preventive measure was good, but the impact to the objects was not fully considered. Fresh edges were exposed when the particleboard was cut. Particleboard is a source of organic carbonyl pollutants, and formaldehyde and organic acid were released from the exposed edges into the microenvironment of the cabinets. These pollutants then reacted with the zinc coating of the locks (manufacturers of metal components such as locks and screws use zinc coatings to improve appearance and resistance to rusting), producing the





Figure 4.2.

(a) Cabinet lock plate covered with fine
 white powder indicative of corrosion by
 organic carbonyl pollutants.
 (b) Corroded
 cabinet handle (note white spots).
 Courtesy of Santa Barbara Museum of Art

change on the active surface that is proportional to the pollutant's concentration. The color is compared to a reference scale provided by the manufacturer. These PSDs are also referred to as colorimetric direct-reading samplers. They are available as diffusion tubes,<sup>3</sup> badges, and test sticks.

**Colorimetric diffusion tubes.** These devices are glass tubes filled with a reagent that reacts with a pollutant, producing a color change along the length of the tube. The length of the color change is proportional to the concentration of the pollutant in the atmosphere being tested. A calibrated scale is printed directly on each tube, indicating readings in parts per million hours (ppm·hr). The concentration (ppm) can be calculated at any time during the exposure period by dividing the tube's reading by the elapsed sampling time (in hours). These



## Figure 4.3.

Cut strips of original laminated particleboard used as earthquake barriers for the cabinet shelves were the source of the organic carbonyl pollutants. Photo: Dusan Stulik © J. Paul Getty Trust powdered corrosion. Analysis showed the powder was a mixture of zinc acetate and zinc formate (Derrick 1988).

The experience of the Santa Barbara Museum of Art illustrates the importance of checking the integrity of metal screws, locks, hinges, and latches on cabinets and other storage systems when accessing a collection. Efflorescence may occur on these items before the objects are damaged, as was the case here. The locks served as serendipitous, in situ passive sampling devices.

After receiving the report about the cabinets' potential risk to the objects housed in them, the museum's director approved funding for modifications to the cabinets that would mitigate the risk. Working under the assumption that the exposed edges of the laminated particleboard strips were the primary source of gases, they were coated to reduce emissions, and the solid doors were modified to screen doors to increase air circulation in the cabinets. Because the cabinets were in a secured vault area, the reduced risk of materials damage more than offset the decrease in the security of the objects.

In 1994 GCI scientists returned to the Santa Barbara Museum of Art to resample the microenvironment of the cabinets in order to evaluate the effectiveness of the mitigation measures. Air quality monitoring confirmed a reduction in organic carbonyl pollutants. Although detectable levels of gases were still present, active corrosion was not observed. In 1997 another sampling campaign showed that the concentrations were still low. Monitoring, mitigation, and testing and retesting are key steps in protecting collections from damage by gaseous pollutants, as is discussed in chapter 6.

The work carried out at the Santa Barbara Museum of Art was a satisfying exchange: the museum protected its collection, and the GCI gained valuable insight into the feasibility of using lock mechanisms and other metal hardware as in situ air quality indicators to identify potentially problematic microenvironments at other institutions. Other conservation professionals have now used this strategy. The Santa Barbara Museum of Art is a success story for preventive conservation and air quality monitoring.

devices offer sampling time flexibility from minutes to hours and even long-term sampling up to twenty-four hours.

To use one of these diffusion tubes, the scored end is snapped off to allow the pollutants to diffuse through the barrier and react with the active material. Reagents are carefully selected not only for distinct color changes but also for specific chemical reactions. However, most reagents react with classes of pollutants; for example, all aldehydes, not just formaldehyde, cause a visible color change. This is interference from within the same class of compounds and is mentioned in the manufacturer's literature.

Direct-reading diffusion tubes are an economical way to monitor environments, but they have drawbacks. In addition to interferences

from compounds of similar chemistry, tubes have relatively high detection limits (80–1200 ppb), although some can be exposed for longer than recommended by the manufacturer, thus increasing the sensitivity. It is recommended that you check with the manufacturer and review the section in chapter 3 on exposure time.

Commercially available quantitative direct-reading diffusion tubes include

- Dräger Color Diffusion Tubes acetic acid, NO<sub>2</sub>, SO<sub>2</sub>
- Gastec<sup>™</sup> Color Dosimeter Tubes acetaldehyde, acetic acid, formaldehyde, formic acid, hydrogen chloride, nitric acid, NO<sub>2</sub>, SO<sub>2</sub>

**Badges.** These PSDs are open-face devices, which means they do not have a diffusion barrier. They are essentially flux meters; the uptake of gas is not limited. Badges are meant to be personal monitors clipped to clothing, but they can easily be used to test museum environments. Most badges are colorimetric PSDs. Commercially available directreading badge monitors include

- AirScan Badges formaldehyde
- ChromAir<sup>®</sup> Colorimetric Badges formaldehyde, NO<sub>2</sub>, ozone, SO<sub>2</sub>
- Dräger Bio-Check badges formaldehyde, ozone
- $EcoBadge^{\mathbb{R}} ozone$
- Leak-Tec<sup>®</sup> badges ozone
- SafeAir<sup>®</sup> Badges formaldehyde, NO<sub>2</sub>, ozone, SO<sub>2</sub>

Test sticks. Similar to their qualitative counterpart, quantitative test sticks produce a color change in the presence of the target gas, but the color change also corresponds to concentration. A commercially available quantitative test stick is

Ozone Test Sticks — ozone

## Laboratory-analyzed PSDs

#### Qualitative laboratory-analyzed PSDs

It may seem pointless to have a PSD analyzed by a laboratory if only qualitative data are obtained. (See table 4.4.) Given that laboratory analysis may be costly, one might wonder how these monitors can be useful. One application is the analysis of the corrosion products on metal coupons, which provides qualitative information about the general classes of gases present and their approximate concentrations. For example, visual inspection of the corrosion on a silver coupon often leads to the conclusion that only sulfide gases are present. Yet laboratory analysis of the corrosion may tell if other gases, such as chlorides, were present. The measurement of the corrosion thickness coupled with the knowledge of the exposure time can determine the extent of the pollution problem (corrosion potential of the environment).

#### Table 4.4.

Selected qualitative laboratory-analyzed PSDs for monitoring museum environments

Sampling Device	Manufacturer's Information	Supplier(s)
Environmental Reactivity CouponsImage: Constraint of the coupon of	<ul> <li>Pollutant(s) detected: Reduced sulfides, nitrogen oxides as nitrates, sulfur dioxide as sulfates, chlorides, organic acids, other acidic gases that react with the metals</li> <li>Exposure time: 30 to 90 days</li> <li>Concentration range: ppb–ppm</li> <li>Cost (2004): \$19–\$300, including analysis</li> <li>Interferences: Not applicable; this is a nonspecific gaseous pollutant test.</li> <li>Analysis: Return to manufacturer as directed.</li> <li>Presence of pollutants is inferred from corrosion; the pollutants are not actually detected.</li> </ul>	Purafil, Inc. www.purafil.com 2654 Weaver Way Doraville, GA 30340 Tel: 404-662-8545 Toll-free: 800-222-6367 Purafil UK Ltd. Astor House 282 Lichfield Rd. Sutton Coldfield, W. Midlands B74 2UG United Kingdom <i>Note:</i> Description of Environmental Reactivity Coupons at www.purafil.com/services.htm#sv_ass

Commercially available qualitative laboratory-analyzed metal

coupons are

• Purafil Environmental Reactivity Coupons — acidic gases from NO<sub>2</sub>, SO<sub>2</sub>; organic acids; H<sub>2</sub>S; chlorides

## Quantitative laboratory-analyzed PSDs

There are many different varieties of quantitative passive sampling devices that require laboratory analysis (see table 4.5). Many of the limitations associated with these devices, such as long exposure times or high detection limits, are a function of adapting devices manufactured for industrial applications to museum monitoring.

Most commercially available devices can be purchased with prepaid analysis done by the manufacturer or supplier; they can also be sent to outside laboratories for analysis or analyzed by an in-house laboratory, if available. University-developed devices are not commercially available. The universities will prepare and analyze the PSDs, or, as indicated below for one of them, users can prepare and analyze their own devices. There are two general types of quantitative laboratory-analyzed PSDs: open-path (Palmes) diffusion tubes and badges.

**Open-path** (**Palmes**) **diffusion tubes.** These diffusion tubes are based on the housing design developed in the 1970s by Palmes et al. (1976) (see fig. 4.4). The basic Palmes housing is a 7.1 cm long tube made of Teflon<sup>®</sup> or an acrylic plastic. It has two airtight caps at each end and an active surface.<sup>4</sup> Because there is no physical diffusion barrier in an open-path tube (the static air in the tube is the diffusion barrier), the ratio of length to outer diameter (usually 1 cm) is critical and controls the rate of diffusion. The active surface is a cellulose pad or a fine wire gauge stainless steel screen or mesh (called a frit) that is chemically treated to trap specific pollutant(s). A cap at one end of the tube holds the active surface in place. The cap on the opposite end of the tube is removed to begin air quality monitoring.



#### Figure 4.4.

Assortment of Gradko Diffusion Tubes for monitoring different pollutants. Courtesy of Gradko International Ltd.

## Table 4.5.

Selected quantitative laboratory-analyzed PSDs for monitoring museum environments

Sampling Device	Manufacturer's Information	Supplier(s)
ChemDisk™ Personal Monitors with or without ChemExpress™ prepaid laboratory analysis Courtesy of Assay Technology, Inc.	Pollutant(s) detected: Acetic acid, formaldehyde (use aldehyde monitor), ozone, total VOCsaExposure time: Acetic acid: 15 minutes to 12 hours Formaldehyde: 15 minutes to 72 hours Ozone: 8 hours VOCs: 15 minutes to 12 hours	Lab Safety Supply, Inc. www.lss.com P.O. Box 1368 Janesville, WI 53547-1368 Toll-free: 800-356-0783 Assay Technology www.assaytech.com
Ø	<b>Concentration range:</b> 1% to 200% of PEL <sup>b</sup> Acetic acid: 1 to 20 ppm Formaldehyde: 0.01 ppm to 1.5 ppm Ozone: 0.01 to 0.20 ppm Total VOCs as hexane: 0.05 ppm to 2 ppm	1252 Quarry Lane Pleasanton, CA 94566 Tel: 925-461-8880 Toll-free: 800-833-1258
The ChemDisk monitor for formaldehyde uses 2,4,- DNPH chemistry.	<b>Cost (2004):</b> 5 samplers with prepaid analysis Acetic acid: \$225 Aldehydes: \$195–\$242 Ozone: \$225 Total VOCs as hexane: \$185–\$387	
	Interferences: None noted. Formaldehyde: None. <sup>c</sup>	
	<b>Analysis:</b> Return as directed; analyze in-house; or submit to an AIHA accredited laboratory. <sup>d</sup> Analytical protocol available. <sup>e</sup>	
GMD Formaldehyde Dosimeter Badge	<b>Pollutant(s) detected:</b> Formaldehyde, acetaldehyde, and other aldehydes	Scott Instruments www.scottinstruments.com
Photo: Cecily M. Gryzwacz © J. Paul Getty Trust	Exposure time: 15 minutes to several days; badges have been exposed as long as 21 days in low-concentration environments Concentration range: Formaldehyde: 15 minutes: 100 ppb 8 hours: 5 ppb	Exton, PA 19341 Tel: 484-875-1642 Toll-free: 800-634-4046
This sampler includes an in situ blank and uses popular 2,4-DNPH chemistry to trap pollutants. It is similar to the SKC UMEx 100 <sup>TM</sup> Passive	Cost (2004): \$178 for 10 badges only; \$853 with prepaid formaldehyde analysis Interferences: None. <sup>c</sup> Analysis: Return as directed; analyze in-house; or send to an AIHA	
Sampler (see below). Grzywacz (1993) reports on the evaluation of the GMD Formaldehyde Dosimeter Badge for use in museum environments. These badges also have been used by the GCI to monitor	<ul> <li>accredited laboratory.<sup>d</sup> Analytical protocol available.<sup>e</sup></li> <li><i>Note:</i> It is difficult to locate the GMD Formaldehyde Dosimeter</li> <li>Badge on the company's website. It is not a "Sure Spot Dosimeter</li> <li>Test Card." To locate on the website:</li> <li>Search for "Paper Tape" technology</li> <li>Dosimeter Badges [GMD Systems]</li> <li>The picture is <i>not</i> the GMD Formaldehyde Badge but GMD direct reading Sure Spot Dosimeter Test Cards for other very toxic gases</li> </ul>	
aldehyde concentrations in gal- leries and display cases at sev- eral museums, including the J. Paul Getty Museum at the Getty Center (see chap. 7) and the J. Paul Getty Museum at the Getty Villa (see chap. 5, sidebar "The Mystery of the Tarnished Silver Stags").	<ul> <li>e.g., phosgene, isocyanates.</li> <li>Download Data Sheet "Dosimeter Badges [GMD Systems]"</li> <li>P. 4 describes the Formaldehyde Dosimeter Badges</li> <li>P. 5 ordering: Kits: Formaldehyde Badge Kit</li> <li>P. 6 ordering: Miscellaneous: Formaldehyde Analysis</li> </ul>	

Sampling Device		Manufacturer's Information	Supplier(s)
Gradko Diffusion Tubes	rtesy of Gradko rnational Ltd.	<b>Pollutant(s) detected:</b> $NO_2$ , $NO$ , $SO_2$ , ozone, $H_2S$ , total VOCs	Gradko International Ltd. www.gradko.co.uk St. Martins House
		Exposure time: 1 to 4 weeks	77 Wales St.
Î		Concentration range: NO <sub>2</sub> , NO, SO <sub>2</sub> , ozone: 0.5–1.0 ppb H <sub>2</sub> S: 0.1 ppb to 60 ppm (can be used for museums: 0.1 ppb = 100 ppt) Total VOCs as hexane: 0.2 ppb to ppm	Winchester Hampshire SO3 0RH United Kingdom Tel: +44 (0) 1962 860331
These open-path diffusi long, 1.1 cm Palmes ho ter 5. The cap is remove diffusion through the st ping surface at the othe	on tubes use the 7.1 cm using described in chap- ed from one end to allow atic air layer to the trap- r end.	<b>Cost (2004):</b> All pollutants except VOCs: \$9–\$29 per sampler with analysis, depending on pollutant. VOCs: \$40 to \$95 per sampler, based on the num- ber of compounds to be analyzed. Analysis is a sep- arate cost.	
		Interferences: None noted.	
		Analysis: Return as directed to Gradko.	
IVL Diffusive Samplers		Pollutant(s) detected: NO <sub>2</sub> , NO, ozone, SO <sub>2</sub>	IVL Swedish Environmental
	Courtesy of IVL Swedish	New: Formic acid and acetic acid	Research Institute www.ivl.se/en/
Environmental Research Institute	<i>Note:</i> IVL is currently validating samplers for formaldehyde. They are developing samplers for hydrogen sulfide and nitric acid.	(Mailing address) Box 210 60 SE-100 31 Stockholm	
These small samplers (approxi- mately the diameter of a U.S. quarter) are marketed for out-		Exposure time: 1 week to 1 month	Sweden
		<b>Concentration range:</b> NO <sub>2</sub> : 0.05 ppb to 418 ppb SO <sub>2</sub> : 0.1 ppb to 75 ppb Ozone: 1 ppb to 100 ppb	Hälsingegatan 43 Tel: +46-(0)8-598 563 00
easily b	e used indoors as well.	Cost (2004): \$77-\$84	
Ferm (1991) developed	the sampler and has	Interferences: None listed.	
investigated it over the Rodhe 1997). For this re plers using the same geo referred to as "Ferm-typ	past decade (Ferm and eason, this and other sam- ometry are frequently be" devices.	<b>Analysis:</b> Return to IVL laboratory as directed.	
The GCI used these sam track $NO_2$ , $SO_2$ , and oze tional study of outdoor for the United Nations.	pplers for several years to one as part of an interna- environmental corrosion		
KEM Medical Vapor-Tra	k®	Pollutant(s) detected: Formaldehyde	KEM Medical Products Corp.
	Courtesy of KEM Medical	<b>Exposure time:</b> 15 minutes to 8 hours; check with manufacturer to confirm longer exposure times.	14 Engineers Lane
ATTA OF	Products, Inc.	Concentration range: 0.75 ppm to 2.0 ppm	Farmingdale, NY 11735 Tel: 631-454-6565
A CONCORPTION OF CONCORPTICA OF CONCORPTICA OF CONCORPTICA OF CONCORPTICA OF CONC		Cost (2004): \$225–\$250 for 4 monitors; includes	Toll-free: 800-553-0330
		Interferences: None noted	www.lss.com
		Analysis: Return as directed.	P.O. Box 1368 Janesville, WI 53547-1368 Toll-free: 800-356-0783

Sampling Device	Manufacturer's Information	Supplier(s)
Ogawa Passive SamplerImage: Solution of the second stress o	Pollutant(s) detected: NO <sub>2</sub> ; NOx (NO <sub>2</sub> + NO); ozone; SO <sub>2</sub> Exposure time: 1 day to 30 days Concentration range: Lower limit 0.2 ppb Costs (2004): Individual Reusable Passive Sampler Set: \$72 Reloading samplers and analysis: \$44-\$57 Interferences: None noted. Analysis: Return as directed; analyze in-house; or send to an AIHA accredited laboratory. <sup>d</sup> Analytical protocol available. <sup>e</sup>	Ogawa & Co., USA, Inc. www.ogawausa.com 1230 S.E. 7th Ave. Pompano Beach, FL 33060 Tel: 954-781-6223
Oxford Brookes University Open-Path Diffusion TubePhoto: Cecily M. Grzywacz © J. Paul Getty TrustPhoto: Cecily M. Grzywacz © J. Paul Getty TrustPhoto: Cecily M. Grzywacz © J. Paul Getty TrustThese devices are shipped in sets of 4 tubes for each location to be monitored.The Oxford Brookes University Biogeochemistry Research Group is the only laboratory that pre- pares tubes to detect hydrogen sulfide and car- bonyl sulfide at parts per trillion, which is the level that poses a risk to silver and photographs.These open-path diffusion tubes were used in the monitoring program at the J. Paul Getty Museum at the Getty Center (see chap. 7).	Pollutant(s) detected (2005): $NO_2$ , $NO$ , ozone, S $O_2$ , organic acids, carbonyl sulfide, $H_2S$ Exposure time: 18 to 38 days Concentration range: $H_2S$ and carbonyl sulfide: low (20–100) ppt to 1000 ppt other pollutants: low ppb to low ppm Cost (2005): Assumes a minimum of 10 sites. These are commercial prices; research programs can qualify for a significant discount (2005): $H_2S: \pounds 210$ Carbonyl sulfide (includes $H_2S$ ): $\pounds 350$ Ozone: $\pounds 120$ S $O_2$ , organic acids: $\pounds 80$ $NO_2$ : $\pounds 80$ Interferences: None. Analysis: Return as directed.	Dr. Simon F. Watts sfwatts@brookes.ac.uk School of Biological and Molecular Sciences, Diffusion Tube Laboratory, Oxford Brookes University, Headington, Oxford, OX3 OBP United Kingdom Tel: +44 1865 483 613 www.brookes.ac.uk/schools/ bms/contact/sfwatts.html
SKC 526 Formaldehyde Passive Sampler for Indoor Air Sampling         Courtesy of SKC, Inc.         Wanufactured by Air Quality         Research, Inc. (Berkeley, Calif.) for         SKC, Inc., this open-path sampler         is 10 cm long and has an outer         diameter of approximately 1.4 cm.         It is useful for monitoring rooms         and galleries and relatively large         display cases (more than 1 cubic	Pollutant(s) detected: Formaldehyde Exposure time: 5 to 7 days (120–168 hr) Concentration range: 0.025 to 1.0 ppm (25–1000 ppb) Cost (2004): \$64 for 2 samplers; does not include analysis Interferences: None. Analysis: Return as directed; analyze in-house; or send to an SKC certified laboratory <sup>f</sup> or another AIHA accredited laboratory. <sup>d</sup> Analytical protocol available. <sup>e</sup>	SKC, Inc. www.skcinc.com/passive.asp 863 Valley View Rd. Eighty Four, PA 15330 Tel: 724-941-9701 Toll-free: 800-752-8472 (USA only)

Sampling Device	Manufacturer's Information	Supplier(s)
SKC 575 Series Passive Sampler for Organic Vapors of SKC, Inc.	<ul> <li>Pollutant(s) detected: Total VOCs<sup>a</sup></li> <li>Exposure time: Up to 24 hours (should be able to increase exposure time and decrease detection limit)</li> <li>Concentration range: Total VOCs as hexane: 10–200 ppb</li> <li>Cost (2004): \$185–\$200 per pack of 5; does not include analysis.</li> <li>Interferences: None.</li> <li>Analysis: Return as directed; analyze in-house; or send to an SKC certified laboratory<sup>f</sup> or another AIHA-accredited laboratory.<sup>d</sup> Analytical protocol available.<sup>e</sup></li> </ul>	SKC, Inc. www.skcinc.com/passive.asp 863 Valley View Rd. Eighty Four, PA 15330 Tel: 724-941-9701 Toll-free: 800-752-8472 (USA only)
SKC Formaldehyde Passive Sampler for Personal Sampling Courtesy of SKC, Inc.	<ul> <li>Pollutant(s) detected: Formaldehyde (available for two ranges: 15-min STEL<sup>g</sup> or 8-hr PEL<sup>b</sup>)</li> <li>Exposure time: 15 minutes to 8 hours</li> <li>Concentration range: 0.2 to 6 ppm</li> <li>Cost (2004): \$139 for package of 5 samplers; does not include analysis.</li> <li>Interferences: None.</li> <li>Analysis: Return as directed; analyze in-house; or send to an SKC-certified laboratory<sup>f</sup> or another AIHA accredited laboratory.<sup>d</sup> Analytical protocol available.<sup>e</sup></li> </ul>	SKC, Inc. www.skcinc.com/passive.asp 863 Valley View Rd. Eighty Four, PA 15330 Tel: 724-941-9701 Toll-free: 800-752-8472
SM™ Air MonitorsSourcesy of 3M Occupational Health & Safety DivisionSubsectionSubsectionThis sampler was used to track total VOCs in the the J. Paul Getty Museum at the Getty Center (see chap. 7) and as part of an American Society of Heating Refrigeration and Air Conditioning Engineers research project on standards for indoor air quality (Grzywacz 2004; Kerr 2004a, 2004b).	Pollutant(s) detected: Total VOCs <sup>a</sup> and formaldehyde Exposure period: Hours to days Concentration range: Formaldehyde: 0.1 to 5 ppm Total VOCs as hexane: low to high ppb Cost (2004): VOCs: \$178 for 10 devices without analysis \$564 for 5 units with prepaid analysis for three gases Formaldehyde: \$151 for 5 units without analysis \$373 for 5 units with prepaid analysis Interferences: None listed. Analysis: Return as directed if purchased with prepaid analysis, analyze in-house, or send to an AIHA accredited laboratory. <sup>d</sup> Analytical protocol available. <sup>e</sup>	Lab Safety Supply, Inc. www.lss.com P.O. Box 1368 Janesville, WI 53547-1368 Toll-free: 800-356-0783 VWR International Scientific www.wwr.com 1310 Goshen Pkwy West Chester, PA 19380 Toll-free: 800-932-5000 SKC, Inc. www.skcinc.com/passive.asp 863 Valley View Rd. Eighty Four, PA 15330 Tel: 724-941-9701 Toll-free: 800-752-8472 (USA only) Additional vendors available from 3M Occupational Health & Environmental Safety www.3m.com/occsafety Toll-free: 800-243-4630/ 888-364-3577

Sampling Device	Manufacturer's	Information	Supplier(s)
UMEx 100 <sup>™</sup> Passive Sampler	Pollutant(s) det not marketed fo to monitor any a completed for g benzaldehyde. S pling rates for o	ected: Formaldehyde. (Although or other pollutants, it can be used aldehyde. Validations have been lutaraldehyde, acetaldehyde, and KC continues to determine sam- ther aldehydes.)	SKC, Inc. www.skcinc.com/passive.asp 863 Valley View Rd. Eighty Four, PA 15330 Tel: 724-941-9701 Toll-free: 800-752-8472
	<b>Exposure time:</b> experience with Dosimeter, it sho sure time up to dated by SKC.)	15 minutes to 24 hours. (Based on the similar GMD Formaldehyde ould be possible to extend expo- 7 days, but this has not been vali-	(USA only)
This device uses paper tape impregnated with	Concentration r	ange: 5 ppb to 5 ppm	
2,4-DNPH and has an in situ blank. Similar to GMD Formaldehyde Dosimeter (see above).	Cost (2004): \$1 include analysis.	34 for pack of 10; does not	
	Interferences: N	one. <sup>c</sup>	
	<b>Analysis:</b> Return send to an SKC AIHA accredited available. <sup>e</sup>	n as directed; analyze in-house; or certified laboratory <sup>f</sup> or another I laboratory. <sup>d</sup> Analytical protocol	
Sampling Device		Manufacturer's Information	Supplier(s)
University of Strathclyde Museum Diffusion Tube Photo: Cecily M. Grzywacz © J. Paul Getty Trust		<b>Pollutant(s) detected:</b> Organic acids (formic acid and acetic acid); formaldehyde.	Dr. Lorraine T. Gibson Lorraine.gibson@strath.ac.uk Department of Pure and Applied Chemistry University of Strathclyde
		Exposure time: 28 days	
This sampler, which uses the 7.1 c	cm long       1 ppm       295 Ca         set of 3 tubes       1 ppm       Glasgo         d.       Cost (Gibson 2005b): £500 to       Scotlar         droxide (KOH)       acids and formaldehyde       Tel: + 4	Concentration range: 0.1 ppb to 1 ppm	295 Cathedral St. Glasgow G1 1XL
Palmes housing, is supplied in a set for each location to be monitored		Scotland Tel: + 44 (0)141 548 2224	
chemistry, and the formaldehyde tubes use 2,4-DN	PH chemistry.	includes analysis.	
The organic acid sampler was designed in response vation community's concern about the damage to organic acids. In 1995 University of Strathclyde res	to the conser- objects from earchers were	<b>Interferences:</b> Organic acids: none Formaldehyde: none. <sup>c</sup>	
the joint recipients of the Jerwood Foundation's Aw Innovation [in Conservation] for "Development of tors for acetic and formic acids" by the Conservation Museum and Galleries Commission, U.K. (Gibson 20	ward for passive moni- on Unit of the 2005).	<b>Analysis:</b> Return as directed. See Appendix 4 for protocols for in- house preparation and analysis, or send protocols with device for	
The GCI collaborated with Gibson and Brokerhof in intralaboratory comparison of these samplers and G. Formaldehyde Dosimeter badges (Brokerhof, Gibsor Gryzwacz 1998). As a result, GCI developed protoco preparation and analysis of these open-path diffusio organic acids and formaldehyde (see Appendix 4).	an inter- and MD a, and ols for the n tubes for	analysis at an AIHA accredited laboratory. <sup>d</sup>	
<ul> <li><sup>a</sup> Most PSDs for VOCs allow the user to specify the gas(es) of interes monitoring purposes, however, <i>total</i> VOCs is most important. Make requested for quantification and that it is reported consistently with same gas, e.g., hexane.</li> <li><sup>b</sup> PEL is the permissible exposure limit defined by OSHA. It is a TWA must not be exceeded during any 8-hour work shift.</li> <li><sup>c</sup> DNPH chemistry that is highly specific for formaldehyde. However, tions of carbonyl compounds may reduce the uptake of formaldehy availability of 2,4-dinitrophenylhydrazine; see Appendix 4, part 5.</li> <li><sup>d</sup> The American Industrial Hygiene Association (AIHA) provides a list ratories on its website, www.AIHA.org, under the link for Laborator</li> </ul>	t. For museum s ure that this is respect to the concentration that high concentra- de by reducing the of accredited labo- y Services.	<sup>e</sup> Analytical protocols are sent with this samp website. These protocols can be used for ir device to an independent laboratory to ass contains GCI-developed protocols for analy DNPH (2,4-dinitrophenylhydrazine) chemis <sup>f</sup> SKC provides a list of AIHA-accredited labo sive sampling products. <sup>g</sup> STEL is the short-term exposure limit, a 15- exceeded at any time during a workday. It Occupational Safety and Health (NIOSH, w	oler and/or are available on the company's 1-house analysis or can be sent with the ure proper analysis. In addition, Appendix 4 zing and preparing selected PSDs based on try and on KOH chemistry. oratories approved for analysis of SKC pas- eminute TWA exposure that should not be is defined by the National Institute of rww.cdc.gov/niosh).

The geometry and transparency of Palmes-based diffusion tubes create certain consequences—slow sampling rate, air velocity effects, and reaction product degradation—that users need to be aware of and compensate for when using them to monitor air quality. (See sidebar "Considerations in the Use of Open-Path (Palmes) Diffusion Tubes.")

Commercially available open-path diffusion tubes include the following:

- Gradko Air Monitoring Tubes NO<sub>2</sub>, NO, SO<sub>2</sub>, ozone, hydrogen sulfide, and total VOCs
- SKC 526 Series Formaldehyde Passive Sampler for Indoor Air Sampling — formaldehyde

Researchers at two universities in the United Kingdom have also developed open-path diffusion tubes specifically for the conservation field. They provide the only samplers capable of detecting reduced sulfides and organic acids at the low concentrations (ppt and ppb, respectively) known to be damaging to objects. The following tubes can be ordered directly from the researchers:

- Oxford Brookes University (Oxford, England) Open-Path Diffusion Tube (the university prepares and analyzes these tubes) — organic acids, hydrogen sulfide, carbonyl sulfide, NO<sub>2</sub>, NO, ozone, and SO<sub>2</sub>
- University of Strathclyde (Glasgow, Scotland) Museum Diffusion Tube (the university will prepare and analyze tubes, or users can follow the instructions provided in Appendix 4) — acetic acid, formic acid, and formaldebyde

**Badges.** Like quantitative direct-reading badges, quantitative badges that require laboratory analysis are meant to be personal monitors clipped to clothing. These badge-type samplers are geometrically different from open-path diffusion tubes. Typically, the active surface is enclosed in a plastic or Teflon<sup>®</sup> housing, and there is a physical diffusion barrier 1 mm to 1 cm above the active surface (see fig. 4.5). Commercially available badge-type PSDs suitable for quantitative air quality monitoring in muse-ums include the following:

- GMD Formaldehyde Dosimeter Badge (can be purchased with prepaid analysis or users can follow the analysis instructions provided in Appendix 4) — formaldehyde, acetaldehyde, and other aldehydes
- IVL Diffusive Sampler acetic acid, formic acid, NO<sub>2</sub>, NOx, ozone, and SO<sub>2</sub>
- Ogawa Passive Sampler NO<sub>2</sub>, NOx, ozone, and SO<sub>2</sub>
- 3M<sup>™</sup> Air Monitors formaldehyde, total VOCs

## Considerations in the Use of Open-Path (Palmes) Diffusion Tubes

Palmes-based diffusion tubes are quite useful for studying museum environments. However, users need to be aware of and compensate for the following characteristics created by the tube's geometry and transparency.

Slow sampling rate. The long path length of the Palmes open-path diffusion tube results in a slow sampling rate, typically about 1 mL per minute. This means that the exposure periods are long, on the order of days or weeks. The need for long exposure times was demonstrated by numerous field tests and chamber studies of the Palmes tube developed at the University of Strathclyde (Glasgow, Scotland) for organic acids and formaldehyde by Gibson et al. (1997a, 1997b) and Gibson and Brokerhof (2001). Exposures of 3 to 5 days at nominal concentrations of acetic acid (less than 100 ppb) did not yield detectable quantities with this device. This occurs because the amount of pollutant trapped on the active surface is near the detection limit. Deployment protocols stipulated by manufacturers and other researchers recommend 7- to 28-day exposure periods (Smith et al. 2000; Torge, Jann, and Pilz 2000; Watts 1996).

Such long-term exposure of a Palmes-based tube can be an advantage for monitoring museum microenvironments such as cabinets and display cases because it allows enough time for the housing's internal climate to achieve pseudo-equilibrium after being disturbed by deployment of the device (for fuller discussion, see chap. 5). The only disadvantage of a long-term exposure could be that visitors will see the samplers. In fact, this could be an opportunity to explain the importance of air quality monitoring.

Air velocity effects. Extremes of air velocity or air movement affect the accuracy of all PSDs, but the open-path samplers are particularly vulnerable because of their long path length and lack of physical diffusion barrier (see Gair and Penkett 1995; Smith et al. 2000; Watts and Ridge 1999). Although air velocity effects are normally not a problem in museum environments, they need to be taken into account when deploying open-path diffusion tubes in areas with extreme air flow, for example, at intakes of HVAC systems or inside fume hoods.

High air velocity creates an eddy at the opening of the tube. Air movement into the tube is no longer controlled by diffusion along the tube's entire length, and consequently the effective path length of the device is shortened ( $L_{true} < L_{physical}$ ). This results in an overes-

timation of the pollutant's concentration. This effect was noted during air quality monitoring at the J. Paul Getty Museum at the Getty Center and was attributed to turbulence effects when open-path tubes were deployed inside the museum's air intake (Grzywacz et al. 2000). Grzywacz and Villalta (2000) confirmed that placing the devices under a shelter reduced the effect of high air velocity.

Reagent and product degradation. Often, the chemical reagents used by PSDs to trap airborne pollutants, as well as the reaction products, are sensitive to degradation by sunlight, temperature, or time. This reduces the sampler's capacity and results in erroneously low readings of pollutant concentrations. Openpath diffusion tubes are especially susceptible because they are usually transparent and exposed for long periods (3 to 4 weeks). Because of temperature sensitivity, manufacturers often recommend storing samplers in freezers or refrigerators before and after exposure. To minimize degradation from sunlight, the PSDs can be placed under an opaque shelter (Smith et al. 2000). This could be the same shelter used to minimize air velocity effects. Some manufacturers specify shelter requirements for their devices.

## Figure 4.5.

Schematic of an Ogawa Passive Sampler, a laboratory-analyzed badge-type PSD. Courtesy of Ogawa & Co., USA, Inc.



<sup>1</sup> Solid Pad

- 4 Coated Collection Filter
- 5 Stainless Screen
- 6 Diffuser End Cap

<sup>2</sup> Pad Retaining Ring

<sup>3</sup> Stainless Screen

In addition to the above samplers, whose usefulness to the conservation community is recognized, the following laboratory-analyzed badges meet the requirements for museum monitoring based on the manufacturers' literature:

- ChemDisk<sup>™</sup> personal monitors acetic acid, formaldehyde and other aldehydes, ozone, and total VOCs
- SKC 575 Series Passive Sampler for Organic Vapors VOCs
- SKC Formaldehyde Passive Sampler for Personal Sampling — formaldehyde
- UMEx 100<sup>™</sup> Passive Sampler for Formaldehyde formaldehyde, acetaldehyde, and other aldehydes

## **PSDs Preferred for Museum Monitoring**

For many years, efforts to improve air quality have been guided by the maxim, use the best available technology. Following this advice for museum monitoring, however, could lead to the erroneous presumption that the most expensive sampler is the best choice and that quantitative samplers are better than qualitative devices. This is not always the case.

Recent technological developments and improvements have equalized all four PSD types (qualitative and quantitative direct-reading PSDs; qualitative and quantitative laboratory-analyzed PSDs) with respect to ease of use, especially in terms of deployment and retrieval. Some may argue that PSDs requiring laboratory analysis are simplest to use. The user only has to expose the monitor, seal it, and return it for analysis. The analytical laboratory determines total exposure time, volume of air sampled, amount of pollutant detected, and the concentration calculations. With most direct-reading PSDs, in contrast, the user must calculate exposure times, compensate for deviations from standard exposure periods,

#### Table 4.6.

Advantages and disadvantages of PSD types

Device Type	Advantages	Disadvantages
Direct-reading PSD	Lower expense per unit Easy to use No analysis required Immediate results	High detection limits Lower accuracy Subject to interferences
Laboratory-analyzed PSD	High accuracy High precision Pollutant specific Low detection limits	Higher cost per unit Complexity of use Results not immediate (weeks)
Qualitative PSD	Indicates overall corrosivity of the environment	Nonspecific: reacts with classes of pollutants, not necessarily individual gases
Quantitative PSD	Pollutant specific	Complex methodology

and determine pollutant concentrations by noting a color change. Because individuals read color changes differently, this can be the source of bias in the results,<sup>5</sup> although having the same person read all devices can minimize this problem. Reading errors, however, usually occur less frequently than errors associated with the device or the methodology. Laboratory analysts can also make mistakes, although laboratories have quality-control checks and assurances to minimize the likelihood that errors are reported to clients.

What about cost? PSDs cost from a few dollars to hundreds of dollars per sampler, but cost can be the least important factor in selecting a device. Generally, the cost and complexity of the device and the technical skill required to use it increase with the device's sensitivity, accuracy, precision, and specificity. Qualitative direct-reading PSDs (e.g., coupons) are easier to use, less complicated, and less expensive than quantitative laboratory-analyzed devices (e.g., open-path diffusion tubes). One might presume that if sufficient funds were available, devices that require laboratory analysis are the best choice. This is not necessarily true: highly accurate and expensive quantitative data are not always necessary to confirm a questionable microenvironment. Satisfactory data can be obtained with the simpler, less expensive direct-reading PSDs.

Table 4.6 lists the advantages and disadvantages of the various categories of PSDs. Tables 4.7 and 4.8 compare the general and specific criteria (cost, ease of use, sensitivity, etc.) to be considered in selecting the appropriate device.

In the end, choosing the best PSD for museum monitoring depends on the specific problem being addressed and the chosen monitoring strategy. These topics are discussed in chapter 5.

## Table 4.7. Comparison of general criteria for passive sampling device types

General PSD Types	Cost	Ease of Use	Precision	Accuracy	Pollutant Specificity	Sensitivity
Qualitative direct- reading PSDs	Low	Easy to complex	Fair	Poor to fair	Poor	Low to Moderate
Quantitative direct- reading PSDs	Low to moderate	Easy	Fair	Fair to good	Poor to fair	Low to high
Qualitative laboratory- analyzed PSDs	Moderate	Moderate	Fair	Fair	Poor	Low to fair
Quantitative laboratory- analyzed PSDs	Moderate to high	Easy to complex	Good	Excellent	Good to excellent	Moderate to high

## Table 4.8

Specific criteria for selecting appropriate passive sampling devices

Direct-reading PSDs						
	Cost	Ease of Use	Precision	Accuracy	Pollutant Specificity	Sensitivity
A-D Strips	Low	Easy	Fair	Fair	Fair	Moderate
AirScan <sup>®</sup> Badges	Moderate	Fair	Fair	Fair	Good	Good
Bio-Check Badges	Low to moderate	Easy	Fair	Moderate	Excellent	Good
ChromAir™ Colorimetric Badges	Low	Easy	Fair to good	Moderate	Low to good	Low
Dräger Color Diffusion Tubes	Low	Easy	Fair	Fair to moderate	Fair	Fair to moderate
EcoBadge®	Low	Easy	Good	Moderate to good	Excellent	Good to excellent
Gastec™ Color Dosimeter Tubes	Low	Easy	Fair	Fair to moderate	Fair	Fair to moderate
Leak-Tec <sup>®</sup> badges	Low	Easy	Fair	Fair to moderate	Excellent	Moderate
Metal coupons	Low	Complex	Fair	Low	Low	Moderate
Ozone Test Sticks	Low	Easy	Fair	Fair to moderate	Excellent	Good
SafeAir™ Colorimetric Badge	Low	Easy	Low to fair	Fair to moderate	Fair	Fair to good

## Laboratory-analyzed PSDs

	Cost (with analysis)	Ease of Use	Precision	Accuracy	Pollutant Specificity	Sensitivity
ChemDisk™ Personal Monitors	Moderate	Fair	Fair to good	Good	Excellent	Fair
GMD Formaldehyde Dosimeter Badge	Moderate to high	Moderate	Excellent	Good	Excellent	Excellent
Gradko Diffusion Tubes	Low to moderate	Fair	Good	Good	Excellent	Excellent
IVL Diffusive Samplers	Moderate to high	Fair	Good to excellent	Good	Excellent	Good to excellent
Kem Medical Vapor-Trak® Badges	High	Easy to fair	Good	Good	Excellent	Moderate to good
Ogawa Passive Sampler	Moderate to high	Fair	Excellent	Good	Excellent	Excellent
Oxford Brookes University Open-Path Diffusion Tubes	High	Easy to fair	Good to excellent	Good	Excellent	Excellent
Purafil <sup>®</sup> Environmental Reactivity Coupons	Low to high	Easy	Poor to fair	Poor to fair	Poor	Poor to excellent
SKC 526 Formaldehyde Passive Sampler For Indoor Air Sampling	Moderate to high	Easy to fair	Good	Good	Excellent	Good
SKC 575 Passive Sampler for Organic Vapors	Moderate to high	Easy to fair	Good	Good	Excellent	Good
SKC Formaldehyde Passive Sampler for Personal Sampling	Moderate to high	Easy to fair	Good	Good	Excellent	Good
3M <sup>™</sup> Air Monitors	High	Easy to fair	Excellent	Good	Excellent	Fair to excellent
UMEx 100™ Passive Sampler	High	Moderate	Good to excellent	Good	Excellent	Good to excellent
University of Strathclyde Museum Diffusion Tubes	High	Easy to fair	Good to excellent	Good	Excellent	Good to excellent

### Notes

- 1. The Oddy test is used to detect potentially dangerous emissions from construction materials that will come in contact with museum collections. For this test, metal coupons are placed in sealed vessels with a sample of the material to be used to make, for example, a cabinet. Off-gassing from the sample is accelerated by adding humidity and heat for twenty-eight days. Corrosion on the coupons indicates release of potentially harmful gases (Oddy and Bradley 1989). (See Appendix 3.)
- 2. Caution must always be used when handling and working with metallic lead, which is an especially hazardous material (NPFA health rating of 4 out of 4). Personal protection equipment must always be worn when handling and working with lead. This includes lead coupons, especially when they are corroded. See articles by C. Stravroudis, WAAC Newsletter, http://palimpsest.stanford.edu/waac/wn/wn19/wn19-2/wn19-205.html and http://palimpsest.stanford.edu/waac/wn/wn19/wn19-3/wn19-307.html.
- 3. Diffusion tubes are passive sampling devices and are not to be confused with *detector tubes*, which are active sampling devices that require a pump. Active sampling is outside the scope of this book.
- 4. Open-path (Palmes) diffusion tubes should not be confused with the quantitative direct-reading Dräger or Gastec<sup>™</sup> colorimetric diffusion tubes.
- 5. Green and Thickett (1993) also demonstrated this for the Oddy test.

## Planning and Conducting an Air Quality Monitoring Program

### **Preliminary Considerations**

## Macroenvironment versus Microenvironment

The considerations for designing air-sampling programs are substantially different from those for macroenvironments, such as galleries and storage areas, and those for microenvironments, such as display cases and storage cabinets. Macroenvironments typically contain several cubic meters of air, whereas microenvironments usually contain less than a cubic meter of air.

Because of dilution effects, macroenvironments usually have lower concentrations of pollutants (see fig. 5.1). GCI surveys of museum environments demonstrated this for organic carbonyl pollutants (Grzywacz 1989; Grzywacz and Tennent 1994). (Chapter 6 explains how to take advantage of this feature to reduce levels of pollutants.) In contrast, because of trapping, the concentration of gases released inside a microenvironment can reach alarming levels, even if it is not airtight. For example,



#### Figure 5.1.

Diagram of relationship between air exchange in museum environments and pollutant concentration (from GCI surveys of indoor-generated pollutants). As airexchange rates increase, pollutant concentrations decrease; this is the situation in macroenvironments. In microenvironments, the air-exchange rates are low and pollutant concentrations accumulate. Drawing by Cecily M. Grzywacz

**Pollutant Concentration** 

acetic acid levels can be as high as 10,000  $\mu$ g·m<sup>-3</sup> or 10 ppm inside museum enclosures made with inappropriate materials (Tétreault 1999).

#### Indoor/Outdoor Pollutant Ratio

A useful tool for monitoring air quality in museums is to simultaneously measure the concentrations of outdoor-generated pollutants, such as ozone, SO<sub>2</sub>, and NO<sub>2</sub>, both indoors and outdoors. The ratio of indoor levels to outdoor levels (indoor/outdoor, or I/O) is a measurement of the effectiveness of a building to protect collections on open display from the outdoor environment. A value less than 1 indicates that the outdoor pollutant level in the museum is less than that outdoors. The smaller the number, the more efficient the HVAC system or building is at keeping outdoor pollutants from entering the museum. A ratio of near 1 or even 0.5 indicates that the building and HVAC system are not successfully keeping outdoor pollutants from entering the space. An I/O ratio greater than 1 indicates that there could be an indoor source of contamination that has been overlooked. This is important information, especially for pollutants considered to be outdoor gases, such as ozone. Typical indoor sources of ozone include air purifiers or photocopiers (see Appendix 1 for a list of other sources).

Outdoor air quality data can be obtained from local regulatory agencies, usually on their websites. For example, the South Coast Air Quality Management District (www.aqmd.gov) monitors and reports outdoor air quality data for the Northwest Coastal Region of Southern California, where both the J. Paul Getty Museum at the Getty Center and the J. Paul Getty Museum at the Getty Villa are located. It is important to use data collected for the same time period as the indoor monitoring exposure period, since the I/O ratio should be calculated from simultaneous indoor and outdoor measurements. Regulatory agencies usually provide hourly or daily levels. To get a time-weighted average for the outdoor readings that corresponds with the TWA reading from the indoor sampler, simply average the outdoor concentrations for the monitoring period of interest. Consider a sampler that gives a reading for a ten-day exposure period. Calculate the corresponding average concentration from the outdoor data by adding the concentrations reported for those ten days and then dividing by the number of days, in this case 10.

An I/O ratio is also especially useful for evaluating two adjacent museum areas, one of which is highly contaminated. For example, consider an art storage room (space A) that is next to a loading dock (space B). If the ratio A/B is much less than 1, we know that the museum's HVAC system is effectively keeping the outdoor pollutants from infiltrating the art storage room.

Similarly, an I/O ratio can be used as a microenvironment-togallery ratio to measure the ability of a display case or cabinet to protect the objects inside from the general museum environment. The pollutant concentration inside a microenvironment should be much lower than that of ambient room air to protect the objects. A ratio greater than 1 indicates the source of contamination is inside the microenvironment. Table 5.1 summarizes how to interpret I/O ratios.

I/O Ratio	Explanation							
	Building interior compared to the outdoor environment	Microenvironment compared to a room environment	Comparison of two related environments: Space A vs. Space B					
I/O > 1 The indoor source emissions are higher than those of the outdoor source.	Source is inside the building.	Source is inside the micro- environment.	Pollutant source is inside space A.					
I/O = 1 Pollutant levels are equal in both areas.	The building and/or the HVAC system is not removing infiltrated outdoor gases.	Air-exchange rate between the two environments is high enough to mix the two air masses (i.e., a leaky micro- environment). Less likely but possible, emissions in the microenvironment are equal to concentrations emitted in the room.	(1) Air exchange between both spaces is the same; or (2) the same pollutant concentration infiltrates both areas; or (3) the sources and effectiveness of materials that remove pollutants from the air (sinks) in both spaces are the same.					
I/O > 0.3 and < 1	30–100% of the outdoor pollutant concentration is infiltrating the building; i.e., the building and the HVAC system remove 0–70% of the outdoor gas.	30–100% of the room pollutant is seeping into the microenvironment.	Pollutant concentration in space A is 30–100% the concentration in space B.					
I/O ≈ 0 or < 0.05 This is the ideal, indicating that pollutant concentrations indoors where objects are housed is very low.	The building and the HVAC system are successfully preventing infiltration of outdoor-generated pollutants.	Very low air-exchange rate between inside and outside environments (well-sealed microenvironment), <i>and</i> there are no pollutant sources inside the microenvironment.	Space A has cleaner air than space B. This is good if objects are in space A, not good if they are in space B.					

#### Table 5.1.

Interpreting Indoor/Outdoor (I/O) Ratios. Both the indoor and outdoor readings must be for the same time period; that is, measurements must be simultaneous. Also, the concentrations being compared must be greater than the detection limit of the sampler used.

#### **HVAC Systems and Pollutant Levels**

HVAC systems are effective air purifiers for museums if they are appropriately designed and properly maintained. A typical HVAC system pulls in outdoor air that is passed through particle prefilters to remove gross particles, is heated or cooled, and is then passed through a final particle filter before being delivered to building rooms (see fig. 5.2). HVAC systems for museums are designed most often to control relative humidity as well as temperature. Controlling temperature and relative humidity along with light and air quality is critical to preserving collections. Air from the galleries is recirculated through the HVAC system. To prevent the buildup of carbon dioxide from visitor and staff respiration, the return air is first mixed with a percentage of fresh air or "make-up air" before being reconditioned.<sup>1</sup>

Air quality from an HVAC system is significantly improved by adding gaseous filtration, and a variety of media with different pollutant affinities are available.<sup>2</sup> If gaseous filtration was not incorporated into the original HVAC design, however, adding it later requires the costly replacement of the system's air handlers to accommodate both gas and particle filters. But several vendors now offer combination chemical (i.e., gas) and particle filters that can be substituted for existing particle filters (see note 2), eliminating the need for an expensive upgrade.





The lack of gaseous filtration increases the likelihood that the I/O ratio of pollutants is near unity; that is, the pollutant concentrations indoors will be nearly the same as those outside the building. With gaseous filtration, the expected levels of outdoor-generated pollutants inside the museum can decrease to less than 5 percent of the outdoor concentration.<sup>3</sup> I/O ratios can be used to track when the gaseous filtration media should be changed. This is done by calculating an I/O ratio when new media are installed to establish a baseline and then comparing this ratio with subsequent ones.

Expensive filtration may not be needed if all objects or collections are housed in microenvironments rather than being on open display. Microenvironments do not have to be hermetically sealed to be effective barriers against gaseous pollutants. However, gaps wider than 1 or 2 cm—in other words, a pencil can be placed through them—will allow cross-ventilation with the gallery air, and HVAC filtration becomes an issue.

## Developing a Monitoring Plan

#### Step 1: Define the Objective

Defining the objective requires that one ask a series of questions: What is the problem or concern? What is the suspected source of the gaseous pollutants? What are the outdoor pollutant levels? What is known about existing environmental conditions inside the museum? What information about the museum environments is missing? Is the air being tested because visible or active corrosion has been observed? Have new display cases or storage cabinets arrived and the suitability of their microclimate is being tested?

Ultimately, the fundamental question comes down to this: What do you hope to learn from air quality monitoring? The easy—but wrong—answer is: the concentrations of all outdoor-generated pollutants inside the museum and all indoor-generated pollutants, measured at the parts per billion level, in all areas of the museum. Such exhaustive monitoring is rarely needed, and it is a waste of precious resources. Hence, the challenge in developing an effective monitoring program is to define a clear objective. Thoroughly question *why* you want to monitor for pollutants and *what* you hope to learn.

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Of course, monitoring for pollutants is imperative if subtle signs of active corrosion are already visible on objects, such as the development of blue, white, or black spots; color changes of pigments, and surface dulling; or paper objects, including labels, that show signs of embrittlement, yellowing, or discoloration. But there are many more reasons to monitor the air quality inside a museum. Although not all-inclusive, the following discussion should help you focus the monitoring program and prevent it from becoming too broad.

# Should you be monitoring for outdoor pollutants that infiltrate the museum?

Outdoor pollutants that enter the museum can pose a risk to objects, not only to those in galleries, but also to those in other open spaces such as storage areas and stacks. Collections on open display face greater risk from outdoor-generated pollutants than those enclosed in microenvironments, such as display cases.

Outdoor air can enter museums in many ways. Situations that warrant monitoring for outdoor pollutants that have infiltrated the museum include the following:

- If the museum has an open floor plan, that is, objects are not enclosed in display cases, and the building relies on natural ventilation with free exchange between indoor and outdoor air.
- If a gallery or storage area has access to an adjacent outdoor area of concern, for example, a courtyard where people are smoking or loading docks where delivery vehicles might be left idling.
- To validate the effectiveness of the museum's HVAC system.
- If there are any other external situations—such as proximity to a transit center, downwind of a paper processing plant, near an airport—that would warrant consideration of monitoring for specific outdoor pollutants inside the museum.

### Should you be monitoring for pollutants generated inside the museum?

A variety of gases are generated inside museums, and their concentrations are almost always higher than that in the outdoor air that infiltrates museums. The types and concentrations of these indoor-generated pollutants are a function of such factors as building materials, display materials, museum activities, number of visitors, and cleaning procedures. Fortunately, of the hundreds of pollutants generated indoors, only a handful pose a risk to museum objects, primarily the organic carbonyl pollutants, nitrogen oxides, ozone, and hydrogen sulfide. General situations that warrant monitoring for indoor-generated pollutants include the following:

- If there are any indications of corrosion, surface alterations, and so on, especially in microenvironments.
- If construction materials have not been tested before use in specific applications. Ideally, all construction materials to

be used in the proximity of objects will first be tested for off-gassing of dangerous pollutants before they are used in construction. A number of standard laboratory tests for construction materials, such as the Oddy test, are described in Appendix 3. Unfortunately, materials testing is rarely done because of a lack of financial resources, experienced staff, and laboratory facilities, as well as time; installation and design schedules are typically too tight to allow materials testing, which can take as long as twenty-eight days. Even when preconstruction tests have been conducted, they are not always carried out for all gases that could pose a risk to specific objects. Further, the tests are low-tech methods for evaluating materials.

• If museum spaces are being renovated. Comparing a baseline air quality reading before alterations with one taken afterward can be used to evaluate the success of the renovation. This before-and-after procedure applies as well to evaluate palliative measures done on a microenvironment, either to improve its seal against exterior pollutants or to reduce or eliminate off-gassing from existing materials.

*Monitoring microenvironments.* Enclosed spaces, such as display cases and storage cabinets, including compact storage units,<sup>4</sup> have special monitoring considerations. Depending on how well they are sealed against infiltration of outside air, these microenvironments can allow dangerously high concentrations of pollutants to build up inside. The following questions will help to determine the need to monitor a microenvironment:

- Is an adsorbent or sorbent, such as activated carbon, being used to control the level of gases in a microenvironment? If yes, monitoring is useful for tracking the effectiveness and/or longevity of the sorbent to determine when it should be replaced or regenerated. (Sorbents are discussed in chap. 6.) If not, and the construction materials are known to offgas potentially damaging pollutants, the use of a sorbent is highly recommended. Testing the enclosure before and after adding the sorbent can help to determine its ability to improve the air quality.
- Have modifications been made to a microenvironment that could affect air quality? If yes, then it should be monitored.
- Has a pollution problem been identified in a display case or storage cabinet? If so, monitoring the empty microenvironment is useful for determining whether the case or its contents are the source of pollutants. Grzywacz (1989) documented instances when empty cases had much higher concentrations of organic carbonyl pollutants than the same cases with objects inside. This suggested that the objects were a sink for the gases and were therefore at risk. Conversely, this information can determine if the objects

themselves, especially wooden objects, are the probable source of contamination. (See sidebar "The Mystery of the Tarnished Silver Stags.")

#### Which pollutants should you monitor?

To help you decide which pollutants warrant monitoring for your specific situation, consult the detailed information on pollutants, their sources, and at-risk materials in Appendix 1.

The kinds of outdoor-generated pollutants of concern to museums depend on the types of fuels used for vehicles and industry in the area, as well as traffic loads, geography, wind patterns, and other weather factors. If the museum is located in an area where alcohol fuels are widely used, then monitoring should also include aldehydes and organic acids, even though they are traditionally considered indoor-generated pollutants. (See chap. 1 for more information about outdoor pollutants.) In addition, local sources should not be overlooked. For example, if the museum is located near industrial sites, it is important to find out which gases they are releasing into the atmosphere and include them in the monitoring program. For example, a paper pulp factory can be a local industrial source of sulfur dioxide (Boye 1987).

For indoor-generated pollutants, consider testing for total VOCs, especially in new buildings, renovated areas, or newly painted galleries, to determine if more specific testing is warranted. As described in chapter 1, the hundreds of pollutants that accumulate inside any building, primarily by off-gassing from construction materials, paints, and cleaners, as well as from human activity, fall in the category of VOCs. The vast majority are low-risk VOCs not known to be a danger to objects, while the few remaining are high-risk VOCs (organic carbonyl pollutants). Some PSDs specifically detect all VOCs and average them into one number, called total VOCs, which is based on the calibration for a specified VOC gas, for example, hexane or toluene.<sup>5</sup> Total VOCs is a good measure of overall air quality. A high reading indicates the presence of significant amounts of indoor-generated pollutants, and these could include high levels of the dangerous organic carbonyl pollutants. Total VOCs can also be used to track changes in the level of indoor-generated pollutants over time. This test is used by many HVAC engineers as a guideline for general air quality (Lull 1990). Sampling for total VOCs was part of the monitoring program for the J. Paul Getty Museum at the Getty Center (see chap. 7). It is important to note that most total VOC samplers cannot detect the small organic carbonyl pollutants. Hence, a low total VOC result does not correlate to a low risk from gaseous pollutants.

## Step 2: Select the Appropriate Passive Sampling Device

A number of factors determine which PSD to use for monitoring. Most important is knowing how low the specific pollutant levels need to be in order to protect the at-risk materials. This will determine the minimum detection limit. Appendix 2 lists target pollutant levels for museums derived from the best available sources. Chapter 1 discusses the limitations of those guidelines and where to get additional information.
## The Mystery of the Tarnished Silver Stags

In the late 1980s, new display cases were built to exhibit silver objects at the J. Paul Getty Museum at the Getty Villa. A sample of the silk brocade fabric selected to line the display cases was submitted to the GCI Museum Research Laboratory for materials testing. It failed a test for reduced sulfur compounds, which are notorious for tarnishing silver. Because of design considerations, the curator still wanted to use that fabric, and the cases were lined with it. As was done for every display case at the museum, trays of activated charcoal were installed underneath the false floors of the display cases to minimize the risk from any emissions inside the case. (Today, better adsorbents are available to remove hydrogen sulfide, such as zinc oxide or activated charcoal impregnated with potassium iodide [see table 6.1].) Trays of silica gel were used to keep the relative humidity low to further reduce the potential for reactions. After a year, the conservation department noticed surface discoloration on silver objects in one display case, in particular, on a pair of objects known as the Biller Stags (fig. 5.3). The stags were tarnishing, and the rogue silk was the presumed culprit.

The GCI was asked to test the microenvironment of the display case containing the stags, and Oxford Brookes University Open-Path Diffusion Tubes for hydrogen sulfide were chosen for the job. The case was tested in two locations, inside the display space with the objects and under the false floor where the sorbent trays were. Although detection of hydrogen sulfide was the expected outcome, this gas was not found in either location, not even at the ppt level. This was good news, yet it did not explain the mysterious tarnishing of the stags.

Along with the diffusion tubes, GMD Formaldehyde Dosimeters had been deployed. These samplers are highly specific for formaldehyde, which Scott (1997) showed also corroded silver. And, in fact, high levels of formaldehyde were detected: 1360 ppb in the display space with the stags, and 930 ppb under the false floor. The difference in the readings was due to the presence of the activated charcoal sorbent under the false floor or to a source in the display space, possibly even an object.

When the museum was preparing for its move to the new Getty Center, art was deinstalled. The stags were packaged in bags and stored for later reinstallation. GCI took advantage of the situation to rule out the display case as the source of the formaldehyde. The case that had held the stags, now empty, was tested again using University of Strathclyde Museum Diffusion Tubes for organic acids and GMD Formaldehyde Dosimeters. But this time, high levels of organic carbonyl pollutants (including formaldehyde) were not detected in the display space or under the false floor.

Still concerned about the mysterious tarnishing, the conservator asked GCI to test the stags in their storage bags. GMD Formaldehyde Dosimeters were placed in the bags for twenty-four hours. An alarming level of formaldehyde was detected. In fact, the concentration was so great that the entire trapping reagent in the PSDs was used up, and the gas had permeated through to the in situ blank of the samplers. One of the bags was retested with a shorter exposure time, and a concentration in excess of 1000 ppb formaldehyde was detected. Next



#### Figure 5.3.

Pair of gilt silver stags, probably used as table ornaments, by Johann Ludwig Biller the Elder, a German silversmith (1656–1732). H: 25 x W: 11<sup>1</sup>/<sub>4</sub> x D: 8<sup>1</sup>/<sub>2</sub> in. Photo: The J. Paul Getty Museum, Los Angeles

the conservator disassembled one of the stags and discovered a wooden dowel that was used to secure the top part of the object to its base. Recognizing the potential risks of wood stored with objects, the conservator isolated the wooden pin in a separate bag and sealed it; then she resealed the stag in its own bag. GCI tested these two bags for formaldehyde. No formaldehyde was detected in the bag containing just the silver object, but more than 1400 ppb of formaldehyde were detected in the bag with the wood. The situation was documented, and the wooden pin was removed from the objects and replaced with an inert support shaft. Few people would have anticipated that the source of formaldehyde would be inside what was considered an inert metal object.

In addition to assuring that the selected PSD can read within the target levels, other factors to consider are how soon the results are needed, accuracy, specificity, cost, and ease of use (see chap. 3 for a discussion of these factors and chap. 4 tables).

The placement limitations and exposure constraints, discussed in the next step, can also be useful in selecting the passive sampling device.

#### Step 3: Identify Locations for PSD Placement

A major advantage of passive sampling for air quality monitoring is that extensive technical skills and sophisticated instrumentation are not required. However, placement of a monitoring device requires proper care and thought. Placement must allow sufficient air circulation for the device to obtain a representative sample of the environment being tested. Placing a PSD inside an object, such as a vase, would not yield a representative measurement because the air circulation is too restricted.

Museum personnel are often concerned that placing sampling devices in plain view will detract from visitors' enjoyment of an exhibition. But this can be an opportunity for education. A brief description of what the devices are for and why air quality monitoring is required can be posted. Most people are not aware of the risk that pollution poses to collections, nor are they aware of the efforts taken to ensure their preservation.

If the devices must be hidden from view, especially if there is a chance that visitors might interfere with the exposure, they should be placed discreetly where there is sufficient air circulation. Frequently, you can take advantage of objects or elements in the display (see sidebar "Suggestions for Hiding PSDs").

**PSD placement in macroenvironments.** In a macroenvironment such as a gallery with good air circulation, pollutant concentrations are more or less uniformly distributed. This makes it easier to obtain reliable readings and minimizes placement concerns. The ideal location is one meter above the floor in a central area of the room, but this is rarely possible. In general, sampling devices can be located anywhere in a macroenvironment space, yet there are some limitations to keep in mind:

- 1. Avoid walls or other vertical structural elements. These may impede air circulation and create concentration pockets.
- 2. Locate PSDs away from areas with high airflow rates, for example, airconditioning vents. If a piece of paper placed in front of the vent is either forcibly blown away or sucked in, the airflow rate is too high.
- 3. In a naturally ventilated macroenvironment, do not place monitoring devices near open doors or windows. This will not yield a representative sampling of the interior air quality.

**PSD placement in microenvironments.** Small, enclosed environments pose special challenges to monitoring air quality. First, most display cases and cabinets are not hermetically sealed, and external or room air can infiltrate them. Consequently, the air exchange between the microenvironment and the external environment may produce variations in the concentrations of gases inside the enclosure being tested. Older case designs frequently were a cabinet with two glass doors that either

slid past each other or opened outward. Gaps between the glass doors are areas where air exchange occurs. This can be good and provide ventilation for cases with high concentrations.

Second, it is not possible to insert a PSD into an enclosure without affecting the microenvironment. Opening the enclosure even a centimeter for a few seconds will cause dilution of the internal air with room air. We want to minimize disturbance of the enclosure's environment. For this reason, it is extremely important to understand ahead of time how the case or cabinet opens so that the most rapid deployment of samplers can be planned. If possible, the case or cabinet should not be open for at least a month before testing the microenvironment. Then when the samplers are quickly deployed and monitoring begins, using longer exposure times that allow an equilibrium to be established can reduce the effects of disturbing the microenvironment.<sup>6</sup> For this reason, it can be beneficial to select devices that have longer exposure times.

## Step 4: Determine the Number of PSDs to Deploy

Commercially available PSDs require only one sampler per location, whether it is a small display case or a large gallery. University laboratories that prepare open-path diffusion tubes, such as at the University of Strathclyde and Oxford Brookes University (see chap. 4), recommend deploying more than one sampler per location, but this is included in the cost.<sup>7</sup>

Blanks. When monitoring with most PSDs that require laboratory analysis, one or more identical devices are left unexposed and desig-

## Suggestions for Hiding PSDs

As long as the PSD is in an area with sufficient air circulation and its active surface is not blocked, placement is limited only by the user's creativity. In a macroenvironment, such as a gallery, possible placements include the following:

- On top of a tall wall, pedestal case, or room divider and out of the reach of visitors. Because heat can affect the sampler's reading, the device should not be placed near overhead lighting or windows.
- Behind signage.
- In a large open object on display, such as a stagecoach, car, or boat.
- Behind a decorative room element, such as a screen or fireplace mantel. During air

quality monitoring at the J. Paul Getty Museum at the Getty Center (see chap. 7) samplers and other equipment were hidden behind an ornamental screen in a corner of the gallery.

- Behind a painting hung on wires. The sampler can be clipped to the wire just below the top of the frame.
- On mounts under a table, behind a clock, behind a vase, on top of a cabinet, on a shelf, or another inconspicuous location.

In a microenvironment, such as a display case, possible placements are the following:

- Behind a large object.
- Discreetly positioned in a dark or back corner.

- Behind "build-ups" or platforms.
- Behind the label of the object on display.

Note: Placing samplers under the false floor of a case is recommended only if the display space is simultaneously tested. If the pollutant source were in the display space itself, the readings under the false floor would be lower than in the display space. On the other hand, exposed boards and/or inferior building materials used to make the false floor could result in higher readings. Also, trays of sorbent to trap pollutants are usually located under the false floor, and placing a PSD in their vicinity would result in artificially low readings of the gases.

nated "blanks." Blanks are used to determine if the samplers are affected during shipment or travel and are referred to as travel blanks. Blanks and PSDs come from the same lot or batch; they are prepared at the same time using the same supplies and reagents. Blanks are handled the same as the samplers, except that they are not opened or deployed. They are shipped with the samplers from the vendor and stored together, and when the PSDs are deployed, the blanks are kept unexposed in an environment with similar temperature and relative humidity. At the end of the monitoring period, both the samplers and the blanks are sent to the analytical laboratory for analysis. The result from the blank(s) is subtracted from the exposed sampler, and this difference is the "blank-corrected" reported concentration.

Suppliers recommend the number of blanks to order, from one to three (blanks are automatically included in each PSD set ordered from a university laboratory). However, cost does become an issue. If two locations are being tested with samplers that cost \$85 each, buying three more for blanks can be cost-prohibitive. In this situation, check with the vendor to see if one blank will suffice.

Some laboratory-analyzed devices, such as the GMD Formaldehyde Dosimeter and the SKC UMEx 100<sup>™</sup> Passive Sampler for Formaldehyde, have blanks incorporated into their housing (i.e., in situ blanks).

A metal coupon should also have an unexposed blank for comparison. The blank is kept in a clean, dark environment. Alternatively, an in situ blank can be prepared by covering half of the metal coupon with  $3M^{TM}$  magic tape,<sup>8</sup> or similar, and burnishing it on the coupon to seal the surface from exposure. This is especially useful when testing display cases because differences between the exposed and blank portions of the coupon can be observed through the vitrine. This reduces the need to open the display case to check the monitoring and thus minimizes disturbances to the microenvironment that would alter results.

#### Step 5: Documentation

Documenting every step and detail of a monitoring program is critical. This record will be an invaluable reference should problems arise with the readings and for planning remediation efforts if unacceptable levels of pollutants are identified. "If you notice it, document it," should be the motto of every monitoring effort. At a minimum, you must keep a record that identifies the type of sampler used, where it was placed, the deployment start date and time, and the deployment stop date and time. Figure 5.4 is a suggested exposure log for documenting a monitoring program.

Deployment start/stop times. It is important to document the start and stop times of a PSD exposure because the laboratory analyzing the device needs to know the volume of air sampled, and this is based on the device's sampling rate and the exposure time. How accurately should you record the start/stop times? If the total exposure period is less than an hour, you should log the time in terms of minutes, using the same timepiece. Less than accurate time recordings can lead to errors in the final result. However, as the exposure period increases, accurately recording the start/stop times becomes less critical. For example, a 1-minute error for a 15-minute exposure is a significant 7% exposure-time error. In

## Figure 5.4.

Sample exposure log for documenting a museum monitoring program. The categories in this suggested exposure log are the minimum data necessary for each location being tested during air quality monitoring. Additional information specific to a given monitoring program can be noted on a separate page.

Ι.	Project:			
	Survey identification number:1			
	Location:			
	Purpose for sampling this location:			
	Has damage been observed in the collection or in this location?			
	Materials			
	What are the primary materials of the at-risk objects in the environment?			
	What construction materials were used in the room or microenvironment?			
	Activities within the Past Six Months That May Affect the Readings			
	List any renovations, including the dates:			
	Macroenvironment: Describe any recent activities that may have affected the air quality, including dates.			
	Microenvironment: When was the last time the enclosure was opened?			
	Has it been at least a month since the microenvironment was disturbed?			
	Has it been at least a month since the microenvironment was disturbed?			
	Has it been at least a month since the microenvironment was disturbed?			
,	Has it been at least a month since the microenvironment was disturbed?			
<u>/</u> .	Has it been at least a month since the microenvironment was disturbed?			
1.	Has it been at least a month since the microenvironment was disturbed?			
<u>/</u>	Has it been at least a month since the microenvironment was disturbed?			
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<u>/</u>	Has it been at least a month since the microenvironment was disturbed?			
<u>^</u>	Has it been at least a month since the microenvironment was disturbed?			
<b>/</b> .	Has it been at least a month since the microenvironment was disturbed?			

contrast, a 5-minute error in recording an 8-hour exposure is only a 1% exposure-time error. Similarly, a 10-minute inaccuracy for a 1-day exposure is only a 0.7% exposure-time error.

	Exposure Data			
Sampler ID:1				
I	Manufacturer's identification number and batch number <sup>2</sup> :			
S F	Sampler deployment Placement: <sup>3</sup>			
	Date and time deployed, indicating A.M. or P.M.:			
1	Temperature:	RH:		
[	Deployment comments, if applicable (e.g., difficulty openi	ing cabinet, odor detected): <sup>4</sup>		
2				
٦	Temperature:	RH:		
Retrieval comments, if applicable (e.g., damage observed not previously recorded, exposed wood surface, sampler partially blocked): <sup>4</sup>				
-	Analycic			
, , , ,	Analysis If laboratory-analyzed sampler To which laboratory:			
	Analysis If laboratory-analyzed sampler To which laboratory:  Date sent for analysis:	Priority delivery (Y/N)		
	Analysis If laboratory-analyzed sampler To which laboratory: Date sent for analysis: Date results received:	Priority delivery (Y/N)		
	Analysis If laboratory-analyzed sampler To which laboratory:  Date sent for analysis: Date results received: If direct-reading sampler	Priority delivery (Y/N)		
	Analysis If laboratory-analyzed sampler To which laboratory: Date sent for analysis: Date results received: If direct-reading sampler Date and time of sampler reading:	Priority delivery (Y/N)		
, , , , , , , , , , , , , , , , , , ,	Analysis If laboratory-analyzed sampler To which laboratory: Date sent for analysis: Date results received: If direct-reading sampler Date and time of sampler reading: Reading result:	Priority delivery (Y/N)		
	Analysis  If laboratory-analyzed sampler  To which laboratory: Date sent for analysis: Date results received: If direct-reading sampler Date and time of sampler reading: Reading result: Notes	Priority delivery (Y/N)		
, , , , , , , , , , , , , , , , , , ,	Analysis  If laboratory-analyzed sampler  To which laboratory:  Date sent for analysis: Date results received: If direct-reading sampler Date and time of sampler reading: Reading result: Notes Record any other observations that might help in interpret during exposure):	Priority delivery (Y/N) ting results (e.g., high traffic area, samplers apparently moved		
/ / / / / / / / / / / / / / / / / / /	Analysis  If laboratory-analyzed sampler  To which laboratory: Date sent for analysis: Date results received: If direct-reading sampler Date and time of sampler reading: Reading result: Notes Record any other observations that might help in interpres during exposure):	Priority delivery (Y/N) ting results (e.g., high traffic area, samplers apparently moved		

- $^2$  Manufacturers usually preassign a sampler number for their own records. The batch or lot may also be documented.
- <sup>3</sup> Document exactly where the sampler is placed: under a table, on top of a display case, behind a painting, in a fireplace, etc. All details are useful, i.e., the south wall, the grand hall, the second floor, the gallery number. See sidebar "Suggestions for Hiding PSDs."

<sup>4</sup> Write down whatever you notice. It may or may not be important later.

#### Construction or renovation details.

Date of renovation. If the microenvironment being tested has been renovated, note when and why it was refurbished. Consider logging answers to such questions as, When did the renovation take place? What initiated it? Who did it? What materials were used? Were they tested before use? After construction or renovation, was time allotted to allow off-gassing before art was moved into the space, and if so, for how long?

*Materials used in the space.* Listing the known construction materials when sampling either a macroenvironment or microenvironment will be useful for identifying the source of detected gases. We know that the major sources of indoor-generated pollutants are woods, paints, adhesives, fabrics, floor coverings, and other materials used in the space (see Appendix 1).

*Macroenvironment documentation.* When testing galleries, storage rooms, and other large, open environments, it is important to document the following three factors that affect the air quality. This will be useful for interpreting the results and recommending actions based on the results.

- 1. Adjacent spaces that affect the macroenvironment. The air quality in galleries next to food service areas, foyers, open patios, loading docks, and so on, can be affected by the activities in these spaces. Observe and note these areas.
- 2. HVAC system information. A museum's HVAC system has a direct effect on preventing outdoor gases from infiltrating the building as well as removing indoor-generated pollutants. The facilities manager or building manager is an important resource to document the operating characteristics of the HVAC system. HVAC documentation should include noting the equipment's age; the temperature and relative humidity set points for the macroenvironment and their range (e.g.,  $\pm$  2°C and  $\pm$  5% RH); how temperature and RH data are collected; hours of operation; percent of fresh (make-up) air and any variation in the amount (e.g., during public hours, closed hours, weather conditions); type of pre- and postparticle filters used, their age, and replacement schedule; installation of gas phase filters, their type, age, and replacement schedule; and air-handler configuration (i.e., are there separate air handlers for areas where collections are exposed; if not, what other areas are served by the same air handler as the room being monitored?).
- 3. Cleaning schedules and supplies. Document when and how frequently galleries are cleaned, by whom, and types of cleaners used.

*Microenvironment documentation.* Because of the ease with which a microenvironment can be disturbed when placing a sampler inside, potentially affecting results, documentation is especially important when testing a small enclosure. The age of the enclosure and the date and time when it was last opened for a prolonged period are two pieces of information about the microenvironment being tested that are essential.

1. Age of the enclosure. Emissions of pollutants inside an enclosure typically decrease with time. For example, emissions of organic carbonyl pollutants from particleboard or plywood decrease significantly in ten to fifteen years. However, solid woods, such as oak, can emit gases for decades and even centuries (Taketomo 1986). If an enclosure is older than fifteen to twenty years and it has not been renovated, detection of high levels of organic carbonyl pollutants would indicate a solid wood source.

2. Date and time last opened for prolonged period. Knowing how long the microenvironment has remained closed and undisturbed after being opened over a prolonged period, even if just an hour or a day, for inspection, art installation, sorbent removal, and so on, is an important piece of information for interpreting monitoring data. Whenever a case or cabinet is opened, internal air is exchanged with room air. The longer it is open, the more air exchange that occurs, and the pollutant concentrations inside the microenvironment are significantly diluted, even if it is opened for as few as five or ten minutes for a small case. Maintaining equilibrium is why sampler deployment must be done as quickly as possible and with minimal opening of the enclosure.

Concentrations of gases build up with time inside microenvironments until equilibrium (really, pseudo-equilibrium) is established, and it is this condition that needs to be monitored for an accurate air quality assessment. The time to reach equilibrium depends on several factors: the off-gassing rate of the pollutant sources; the leak rate (air exchange rate) of the enclosure; and the gas removal rate due to absorption by or reaction with surfaces, including walls, sorbents, and even the objects themselves. Ideally, the microenvironment should be sealed for as long as possible before monitoring, but this is not always feasible. The GCI recommends that enclosures be sealed for at least a month prior to air quality monitoring. Although equilibrium may not be fully established by that time, the concentrations obtained are still meaningful.

If an enclosure has not been sealed long enough to reach equilibrium, monitoring results will be affected. Detecting low pollutant levels in this instance does not necessarily mean that the environment is safe for the objects inside. On the other hand, if high pollutant concentrations are nonetheless detected, then the levels at equilibrium would most likely be much higher, and the concern would be greater than the numbers alone indicate. PSDs that are deployed for one day or less are more susceptible to measuring artificially low pollutant concentrations with short enclosure sealed times. For this reason, samplers with longer exposure times, such as open-path diffusion tubes that are deployed for a month, are advantageous and minimize the effect of short sealed times.

#### Step 6: Inform Museum Personnel

It is extremely important that all relevant museum personnel (curators, directors, exhibition staff, conservators, security, and housekeeping) be informed of the monitoring program before testing begins. For example, if preparation staff are not notified, samplers may be lost when exhibitions are deinstalled. Similarly, cleaning crews may sweep away

## Deployment and Retrieval of PSDs

The guidelines presented here are for the deployment and retrieval of two types of PSDs: badge-type devices and open-path diffusion tubes, represented, respectively, by the GMD Formaldehyde Dosimeter and the open-path diffusion tubes developed by the University of Strathclyde and Oxford Brookes University. These two types of samplers were chosen because they illustrate extremes in geometry. Additional information about these devices is found in tables 4.5-4.8. GCI-developed protocols for analyzing GMD Formaldehyde Dosimeters and for preparing and analyzing the University of Strathclyde diffusion tubes are found in Appendix 4.

## GMD Formaldehyde Dosimeter

GMD Formaldehyde Dosimeters are shipped in individual metal foil bags marked with the batch number, expiration date, and badge number. The bags come with sealing clips, which are white plastic rods with a cylindrical bar clasp. When the GMD Formaldehyde Dosimeter is opened or ON, only half of the chemically treated tape is exposed; the other half is an in situ blank. Samplers should be stored in the freezer (T  $\leq$ 4 °C) until ready for use. They have a three- to six-month shelf life.

Before deployment, examine the location to be tested and determine where the badges will be placed. This is especially important for a microenvironment, which must be disturbed as little as possible when deploying samplers.

## Deployment

• When ready to deploy the sampler, trim the metal bag along

one edge and remove the badge. The bag also contains a metal screen with a strip of orange paper; this is a scavenger used to absorb contamination during transit. Do not handle the scavenger; leave it inside the bag, place the bag inside a ziplock plastic bag, and return to the freezer (save the white sealing clip for later).

- On the exposure log for your monitoring program, note the badge number, lot number, test site, date, and time of deployment, as well as temperature and relative humidity. In addition, write the test site, date, and time on the tag attached to the sampler.
- Slide the badge cover to the open position (fig. 5.5) and place the sampler in the desired location, face up. If the badge is deployed in a microenvironment, such as a cabinet, try to place it away from any joints or cracks that might allow outside gallery air to seep inside. Also make sure that a displayed object does not block the diffusion barrier.
- Exposure times for this device range from eight hours to five days. In most situations, one to three days are sufficient. Actual times vary with specific monitoring situations; use your best judgment.

## Retrieval

• Remove the badge from the deployment site, slide the cover shut, and note the date and time on the badge's tag as well as in the exposure log. This duplicate information prevents mistakes when the sampler is analyzed in the laboratory.

- Document the final temperature and relative humidity on the exposure log and, if available, the average temperature and relative humidity during the exposure.
- Place the badge in the foil bag it came in; the bag should still contain the scavenger. Secure the bag with a sealing clip as follows: wrap the cut end of the bag around the white plastic rod, and snap on the cylindrical bar clasp so it is snug and provides an airtight seal.
- Return the bag to the freezer until the device is ready for analysis, which should occur as soon as possible and at least within thirty days of exposure.
- If the badge is to be mailed to an outside laboratory for analysis, do this as soon as possible and use an overnight



## Figure 5.5.

GMD Formaldehyde Dosimeter badges: documentation label (top); diffusion barrier covered = OFF position (left); diffusion barrier open = ON position (right). Photo: Cecily M. Grzywacz © J. Paul Getty Trust delivery service to ensure that it is not exposed to high temperatures for significant periods. Include either the vendor-supplied protocol or the protocol in Appendix 4 with the shipment if the laboratory is not familiar with the analytical method.

## **Open-Path Diffusion Tubes**

The passive sampling devices developed by both the University of Strathclyde and Oxford Brookes University are based on the Palmes open-path diffusion tube housing. These samplers are 7.1 cm long, 1.1 cm outer diameter acrylic tubes capped at both ends. One cap holds a trap for the pollutants, and the other cap (clear) is removed during exposure. Gases diffuse through the static air layer of the tube and are retained at the active surface.

University of Strathclyde tubes can be purchased directly or prepared in-house following the protocols in Appendix 4. Oxford Brookes University tubes must be purchased directly. Once the tubes are prepared or received from the university, they must be stored in a refrigerator.

## Deployment

• The University of Strathclyde recommends two samplers and one blank for each location. Oxford Brookes University supplies three samplers and two blanks for each location. Both universities charge by the location, not the tube. Before deploying the samplers, record on the exposure log the tube number, location, placement, and start date and times as well as temperature and relative humidity.

- When ready to monitor, remove the clear cap (fig. 5.6) and place the tubes such that the open end is not blocked by an object, mount, wall, and so on. Since diffusion is independent of gravity, tubes can be placed either horizontally or vertically without affecting the sampling rate. However, Oxford Brookes University recommends mounting its tubes vertically, with the open end facing down to prevent particles from settling in the sampler.
- Place the unopened blanks with the samplers or, if that is not possible, in an environment similar—for example, the same average temperature and relative humidity—to the location being tested.
- The typical exposure period for an open-path diffusion tube is twenty-eight days, although ten to fourteen days can usually provide sufficient concentration data. Remember, however, that shortening the exposure reduces the amount of a gas trapped on the active surface and, as a result, increases the device's detection limits.

## Retrieval

- At the end of the deployment, replace the clear cap on the tubes. Note the time and date of retrieval. Store the samplers (and blanks) in the refrigerator until analyzed, which should be done as soon as possible and no later than six weeks after exposure.
- Send the exposed tubes and blanks by overnight delivery service to the analytical laboratory. Oxford Brookes



#### Figure 5.6.

University of Strathclyde Museum Diffusion Tubes (MDTs): MDTs are uncapped or opened for exposure. Bluecapped tubes are used to detect organic acids (left); red-capped tubes detect formaldehyde (right two samplers). Photo: Cecily M. Grzywacz © J. Paul Getty Trust

> University tubes and tubes ordered from the University of Strathclyde must be returned to the respective university for analysis. If tubes were prepared using the protocol in Appendix 4, send the exposed tubes and blanks for analysis, along with the protocol provided in Appendix 4, to a commercial laboratory.

samplers when cleaning galleries if not warned ahead of time. Security should be informed of the monitoring and sampler locations interspersed throughout the collection so that curious patrons do not disturb them. Moreover, if all museum personnel members are informed, they may be able to contribute important information that needs to be documented that otherwise would not have been considered, obtained, or included.

#### Step 7: Conduct a Premonitoring Walk-through

At this point, you have determined the type of samplers to use for monitoring and where they will be placed. An exposure log has been set up to document as much information as possible about the monitoring effort. All relevant staff have been notified about when monitoring will commence and cautioned about disturbing the samplers. But before testing begins, a premonitoring walk-through is advisable. This walk-through provides a last opportunity to review every step of your plan and modify it if need be.

#### Step 8: Deployment and Retrieval of Samplers

The following discussion covers general PSD deployment and retrieval considerations, although the manufacturer's instructions should be the primary guide. The sidebar "Deployment and Retrieval of PSDs" provides specific instructions for two example PSDs: a commercial badge-type device and a noncommercial open-path diffusion tube.

**Deployment.** Figure 5.7 demonstrates the proper deployment of different types of samplers. When deploying directional PSDs, such as badges, it is important to ensure that the collection face or side is open to the environment. Likewise, the open end of tube devices must be placed such that walls or objects on display do not block them.

*Retrieval.* Because there are no concerns about disturbing an enclosure's equilibrium after monitoring has ended, removing samplers from microenvironments is straightforward. The case is opened, the date and time are documented, and the samplers are removed. This is a good time to inspect and note any observations of the materials or objects in the enclosure as well as to photodocument the placement of the samplers.



### Figure 5.7.

Proper deployments of University of Strathclyde Museum Diffusion Tubes (right) and GMD Formaldehyde Dosimeter badges (left) in a Getty Museum decorative arts case. The flat devices were a prototype monitor developed by the Netherlands Institute for Cultural Heritage. Photo: Cecily M. Grzywacz © J. Paul Getty Trust *Direct-reading devices*. Direct-reading devices usually involve a color change or color development. The chemical giving rise to the color change may not be stable with respect to time, light, temperature, or relative humidity. Hence, the results should be read immediately and documented. It can be useful to photograph the exposed direct-reading PSD next to an unexposed device to illustrate the change.

*Laboratory-analyzed devices.* PSDs that require laboratory analysis must be closed, sealed, and prepared for shipment. Follow the manufacturer's instructions for closing the PSD, which terminates the exposure and stops the collection of gases. Typically, closure involves sliding a built-in cover over the diffusion barrier for a badge-type device, capping an open tube, or putting the entire device into a supplied airtight bag or container. To preserve the integrity of the sampler and the trapped analytes until shipment, PSDs should be stored in a freezer or refrigerator, according to the manufacturer's specifications. Laboratory-analyzed devices are usually sent by overnight delivery to the analytical laboratory.

Considerations for laboratory analysis of PSDs. Keep in mind that most laboratories that quantify PSDs do so to determine human exposure to hazardous chemicals in the workplace, not to determine which pollutants are in museums. Thus, not all laboratories are familiar with the needs of conservation. The PSD exposure times used in museum monitoring are typically longer, and the concentrations being detected are frequently much lower. The manufacturer's laboratory or a certified contract laboratory that routinely conducts these types of analyses usually provides the best analytical results. Table 4.2 includes information on laboratories for the analysis of the different devices. Some vendors, such as SKC, Inc., provide a list of regional accredited laboratories certified to analyze specific SKC devices. Other independent private or university laboratories can be used as well, especially for monitors that include analysis protocols.

**Communicating with the laboratory.** Although an analytical laboratory may be fully competent, the conservation professional can help to assure useful results by communicating with the laboratory's manager or analyst prior to analysis. Explain how air quality affects the preservation of collections and why the samples being analyzed are pertinent to your specific monitoring objective. Most laboratory scientists are intrigued by the melding of conservation and science, and an initial dialogue with the analyst may inspire interest in the project. Frequently, the analyst will take extra time to understand novel situations and even modify protocols to provide better information for the purpose at hand. It may be helpful to ask a conservation scientist, if available, to communicate with the laboratory. The scientist often can provide the best explanation of the reasons for the analysis and what nuances may be important.

*In-house preparation and analysis of PSDs.* For museums equipped with laboratory facilities, certain commercial PSDs can be analyzed in-house following the protocols provided by manufacturers and vendors. The protocols are sent with the samplers and/or are available on the company's website.

In addition, the GCI developed protocols for analyzing carbonyl pollutants extracted from GMD Formaldehyde Dosimeters and

similar PSDs that are based on DNPH (2,4-dinitrophenylhydrazine) chemistry. In collaboration with Lorraine Gibson of the University of Strathclyde, who developed the Museum Diffusion Tube for organic acids, the GCI Laboratory wrote protocols for both the preparation and the analysis of these tubes based on Gibson's procedures. All protocols are described in Appendix 4.

## The Next Steps

Chapter 6 examines how to interpret the results of an air quality monitoring program. It also explores mitigation considerations if monitoring uncovers a problem with pollutants and introduces the concept of preventive conservation to avoid problems in the first place.

## Notes

- 1. The American Society of Heating, Refrigerating, and Air-Conditioning Engineers has developed guidelines for HVAC systems for museums, galleries, libraries, and archives (Baker and Grzywacz 2003).
- Information about HVAC filters is available from the National Air Filtration Association: www.nafahq.org. NAFA has also written best practices guidelines for libraries, archives, and museums. Information about the new combination gas– particle filters is available from the following vendors: Purafil, www.purafil.com; 3M, www.3M.com; Air Filter Sales, www.airfiltersales.com. Additional vendors can be found at www.thomasnet.com, an online catalog of vendors that are listed in the Thomas Registry Directory (www.thomasregistrydirectory.com).
- 3. Ozone can sometimes be reduced, but not eliminated, even without gas filters. It is a highly reactive pollutant that is suspected of reacting with the HVAC ductwork and being eliminated before the conditioned air is delivered throughout a building. It is also unstable and will decay to ordinary oxygen. I/O ratios can be 0.7 or lower, indicating that the ozone level in the conditioned air is 30 percent less than the outdoor level. This presumes that there is no natural ventilation such as open doors and windows.
- 4. When collapsed, compact storage units can be considered cabinets; that is, except for the open aisle, the units are essentially storage cabinets with their own micro-environment.
- 5. When tracking total VOCs, it is important to use the same laboratory for analysis. Differences in analytical methods, calibrations, and techniques can affect the results.
- 6. Gibson (1999a) describes this as a *pseudo-equilibrium*, since it is nearly impossible to determine when a true equilibrium is achieved. Some of these points are discussed by Grzywacz (1995a) and Grzywacz and Stulik (1992). Although these papers emphasize active sampling, the information can be applied to passive sampling as well.
- 7. The universities will automatically send the correct number of samplers with each order, based on the number of locations to be monitored.
- 8. Do not use cellophane tapes or similar transparent tapes because they degrade and become an ineffective seal on the coupon.

## Interpreting Results and Mitigation Considerations

Conservation scientists would like to be able to offer museum professionals clear-cut instructions on how to interpret the results of air quality monitoring programs. Unfortunately, given the complex nature of pollutant interactions with cultural materials, the link between the concentrations detected and the risk to objects is not yet—and perhaps never will be—completely understood. Even conservation scientists themselves do not necessarily agree on acceptable levels for pollutants in museums. However, enough information is now available to offer museums reasonable guidelines with which to protect their collections. As ongoing research reveals new insights into how pollutants interact with cultural materials, these guidelines will be refined.

Numerous criteria influence how air quality data are evaluated. This is because each museum situation is unique in terms of geographic location, the nature of outdoor pollutants, the macro/microenvironments inside the museum, collections characteristics and conservation history, construction and renovation history, and financial resources. Hence, interpreting monitoring results involves the personal judgment of the museum's professional staff as much as it involves guidelines.

This chapter explores issues related to interpreting air quality monitoring results as well as mitigation efforts if a problem is detected. It also introduces the concept of preventive conservation, a global way of thinking that helps museums to accomplish their duties as caretakers of cultural heritage by averting damage to their collections in the first place. Hatchfield's 2002 book, *Pollutants in the Museum Environment*, should be consulted for additional information on this topic.

## Interpreting the Results of Air Quality Monitoring

Everything discussed in the preceding chapters on gaseous pollutants, passive sampling, and conducting a monitoring program comes into play in interpreting the air quality results. Two important references are Appendix 1, an in-depth compilation of gaseous pollutants, their sources, and at-risk materials, and Appendix 2, a table of target standards for key gaseous pollutants found in museums, based on the best available sources. However, arriving at a reasonable interpretation of the results begins with asking questions to put the numbers into perspective.

Do the results provide useful information? Make sure the sampler selected for the monitoring program can detect the pollutants at levels that put your collection at risk. Hydrogen sulfide is a good example. Most if not all commercially available PSDs for  $H_2S$  have ppm detection limits. If these samplers do not detect any  $H_2S$ , it does not mean that there is no risk to a silver collection, because damage occurs at ppt levels. Similarly, if a Dräger Color Diffusion Tube for acetic acid is exposed for eight hours and no color change is observed, it does not mean that a collection of ceramics is not at risk from acetic acid. It only means that less than 1.3 ppm of this pollutant was detected. The sampler is not detecting the gas in the range of concern for this material.

Do the readings make sense? If a reading seems questionable, consult the exposure log for your monitoring program to see if anything happened that would explain it. Was a new cleaning solvent being used in the area being tested? Was an electrostatic air purifier installed that could be generating ozone? Could the microclimate have been disturbed during the sampling period? Did the HVAC system shut down for service? Were there a few days of extremely high outdoor pollution levels? A questionable reading was encountered during the monitoring program for the J. Paul Getty Museum at the Getty Center, but a review of the exposure log explained it (see sidebar "The Importance of Documentation").

Are the readings applicable to the situation at hand? For example, the presence of formaldehyde in a microenvironment does not necessarily mean that the objects are at risk if the materials in the collection do not react with formaldehyde. However, if an oxidant such as UV light or peroxide is also present in the microenvironment, formaldehyde

## The Importance of Documentation

While air quality was being monitored during construction of the J. Paul Getty Museum at the Getty Center, a critical event occurred as art was being installed. This event could have resulted in misinterpretation of the air quality data—and raised alarm over risk to the collections—if it had not been accounted for in the monitoring documentation.

Passive sampling was being used to obtain time-weighted average monthly readings for hydrogen sulfide. In the middle of July 1997, the HVAC system's boilers were being cleaned off-line when a shutoff valve failed. A reaction in the lines generated hydrogen sulfide, and high concentrations of this gas were released into the galleries. The incident and its short duration were duly recorded on the exposure log maintained for the monitoring program.

When the sampler results came back from the Oxford Brookes University laboratory, they showed that the average monthly readings for hydrogen sulfide were very low, typically below the detection limits of the samplers, except for the month of the accident. That reading was 5 ppb, which would have been alarming if both staff and collections had been exposed to this level of hydrogen sulfide every day for this period. In fact, the high concentrations existed only briefly. The HVAC system rapidly removed the caustic airborne gases, and what had been released into the galleries was eliminated within hours.

The monthly reading in question was correct, but documentation of the accident recorded in the exposure log confirmed that it did not accurately reflect reality. The reading was skewed because of the nature of time-weighted averages: the extreme spike that occurred for a few hours on the day of the accident was averaged over the entire monthly exposure period. The reading for that particular month was an anomaly, and therefore the data were discarded. can be converted to formic acid, a more aggressive gas that may put the collection at risk.

Do the readings warrant additional monitoring? For example, a high level of total VOCs indicates the presence of a large amount of indoor-generated pollutants, most of which are low-risk. However, organic carbonyl pollutants could also be present, and if objects are at risk for these pollutants, additional monitoring is warranted with devices specific for these high-risk gases.

## A Problem Is Detected: The Case for Mitigation

Ideally, we would like air quality monitoring to confirm that high concentrations of a potentially dangerous pollutant are not present in the environment being tested. At the very least, if troublesome gas levels are detected, we would like to be able to eliminate the source, along with the problem. But when this is not possible, either because the source cannot be identified or because it cannot be removed for logistical reasons, the next step—an urgent one—is mitigation, even though our understanding of how gaseous pollutants damage cultural materials is still incomplete. We cannot let unanswered questions prevent us from protecting collections and archives from the risks of pollution. Museum professionals are charged with ensuring that objects are preserved to the best of their ability today, even though tomorrow will bring new findings and discoveries about pollutants that may alter our understanding of mitigation measures.

A number of mitigation measures can be implemented. For example, the pollutants can be isolated from the collection by physical or chemisorption<sup>1</sup> on an adsorbent or reactive surface. Isolation can also be accomplished by increasing ventilation or air-exchange rates to dilute pollutant concentrations. Also, lowering the temperature and/or the relative humidity can slow the reaction rate between the object and the gases. If the air quality cannot be improved or the risk reduced, then limiting the amount of time a susceptible collection is exposed to deleterious pollutants can minimize adverse effects. This is common practice for light-sensitive materials such as silk, paper, colorants, or parchments.

Any improvement in air quality is valuable, and mitigation steps are additive. In fact, the most effective solution is usually implementation of a combination of steps. Metro and Grzywacz (1992) demonstrated this by measuring the cumulative air quality effects of using a barrier foil, an absorbent board, and a sorbent to control pollutants in an experimental setting at the J. Paul Getty Museum at the Getty Villa. The J. Paul Getty Museum Preparation Department and GCI Science investigated mitigation strategies using three identical mock-up display cases and one identical control case, built with plywood bases and acrylic vitrines. In the first display case, a barrier foil of aluminum laminated with plastic was applied over the wood base to block emissions of gases. In the second display case, in addition to the previous mitigation measure, a chemically treated board to absorb acidic gases was used to build the object platforms ("build-ups"). In the third display case, in addition to

the previous two mitigation measures, a tray of activated carbon was placed under the build-ups to adsorb reactive gases.

Air quality monitoring was conducted at one week, two weeks, and five weeks. There was a 30 percent reduction in organic carbonyl pollutants in the first display case (barrier foil only), a 67 percent reduction in the second display case (barrier foil plus chemically treated platforms), and a 90 percent reduction in the third display case (barrier foil plus chemically treated platforms plus activated charcoal sorbent). As these results show, additive mitigation measures were needed to eliminate the damaging gases.<sup>2</sup>

Even when no funds are available for major mitigation measures, modest steps can be taken to reduce the risk to objects. This was the case at the Santa Barbara Museum of Art, described in chapter 4, sidebar "Monitoring in Action."

Whenever possible, mitigation decisions are best made by a consensus of all personnel responsible for the care of the collection, including conservators, curators, collections managers, museum administration, designers, scientists, and even the owners of the affected objects if on loan to the museum. Each has concerns and knowledge that can be incorporated into a plan of action.

#### Mitigation Steps to Consider

Although an in-depth discussion of mitigation is beyond the scope of this book, this section highlights some of the measures to be considered. *Pollutants in the Museum Environment: Practical Strategies for Problem Solving in Design, Exhibition, and Storage* (Hatchfield 2002) is a good reference on mitigation, as are Tétreault's *Airborne Pollutants in Museums, Galleries and Archives: Risk Assessment, Control Strategies and Preservation Management* (2003a) and "Display Materials: The Good, the Bad, and the Ugly" (1994).<sup>3</sup>

Before adjusting environmental parameters, either in a macroenvironment or in a microenvironment, it is imperative to consider the ramifications in order to ensure that modifications to improve air quality do not create a greater overall risk for the objects. The precarious balance of all of the risks to objects is a challenge for collections managers. Preservation is frequently a compromise to reduce the greater of evils.

## Mitigation for macroenvironments

• If extremely high levels of total VOCs or other indoor-generated pollutants are detected in a macroenvironment such as a gallery or a storeroom, reduce concentrations by increasing ventilation to dilute indoor air with outdoor air. This can be accomplished by increasing the HVAC airexchange rate or, in naturally ventilated buildings, by opening doors or windows. *Caveat:* If the outdoor air is very polluted, do not dilute indoor air with it unless there are gaseous filtration media in the HVAC system. Likewise, for naturally ventilated buildings, you have to weigh the benefits of decreasing the level of indoor-generated pollutants by increasing the amount of outdoor-generated pollutants allowed inside the museum.

• If high pollutant readings are found in a recently constructed or renovated gallery or storeroom, allow additional curing time before moving objects into the area. At-risk objects could also be placed in protective display cases, which would isolate them from the poor air quality in the room. Construction materials should be pretested for harmful emissions so that objects are not exposed to new risks from off-gassing. Appendix 3 lists several useful tests for construction materials. New construction materials with low or zero VOC emissions are available (see third item under "Mitigation for microenvironments").

If a gallery or other macroenvironment with high pollutant readings is to be renovated, use the new low-VOC paints and adhesives. Paints with pollutant adsorbents added are also available. Although specifically designed to improve air quality with respect to people, these paints will work just as well for collections. Furthermore, additional walls can be erected to act as sinks for the gases, as long as the materials have been pretested to confirm that they themselves do not off-gas dangerous levels of pollutants. Adding walls in a gallery is often done to guide visitors through a new exhibition, and they can serve a double purpose for pollutant control.

• Install an HVAC system with gaseous filtration or upgrade an existing system to include gaseous filtration (see HVAC discussion in chap. 5).

## Mitigation for microenvironments

- To dilute pollutant concentrations in a microenvironment, increase its air-exchange rate. This can be done simply by drilling a couple of holes in the vitrine. More sophisticated methods might include using small, quiet computer fans to circulate the air out vents added to the case. *Caveat:* As in the first item under "Mitigation for macroenvironments," it is critical to evaluate the repercussions of environmental changes for at-risk objects, since increasing an enclosure's air exchange rate will also affect temperature and relative humidity control.
- If high pollutant concentrations are detected in a microenvironment that was recently constructed or renovated, allow more curing time before installing objects and sealing.
- If resources are available, rebuild problematic display cases or cabinets with materials that do not off-gas dangerous pollutants. Manufacturers have developed new products, including pressed-wood boards, plywoods, and composite



#### Fig. 6.1.

Kunstkammer display case showing access to the space under false floor. Photo: Brian Considine © J. Paul Getty Trust boards, with lower VOC emissions by reducing the amount of urea-formaldehyde resin binder. Some manufacturers have changed binders altogether to eliminate the health risk from formaldehyde off-gassing. A few of these products are marketed directly to the conservation field, such as wood composite boards known as Medex<sup>®</sup> and Medite II<sup>®</sup>.<sup>4</sup> Be aware that just because a product has little or none of one pollutant, it does not mean that it has no harmful gases; for example, Medite II may not release formaldehyde, but there is still a risk from acetic acid released from the wood.

- If rebuilding cases and cabinets is not an option, isolate the materials that are pollutant sources inside a microenvironment with products such as foil-laminate barriers (e.g., Marvelseal<sup>™</sup>) or buffered mat boards. Foil laminates are designed to be heat-sealed over the entire surface to reduce emissions, but these products are far less effective if they are only taped down at the edges. Such time-saving measures may be ineffective when accidental punctures of the laminate allow the gases to enter the display case. Barriers are usually not aesthetic but can be hidden under fabric. A low-cost but less effective alternative to foil laminates is heavy-duty aluminum foil sold in grocery stores (Grzywacz and Alten 1999).
- Remove dangerous gases in microenvironments with sorbents. Several products are available, although most are nonspecific. Table 6.1 lists the disadvantages and advantages of a few common sorbents used in conservation. To answer questions about the use of sorbents, the GCI evaluated their performance in a research program conducted from 2001 to 2003 (Druzik 2001, 2003).

To be effective, sorbents must remove dangerous pollutants faster than the gases can react with the objects.<sup>5</sup> Typically, trays filled with sorbent are placed under a display platform or false floor that has holes or other perforations to facilitate air movement (see fig. 6.1). Trays can also be located under the build-ups for the objects. Some museums place Petri dishes of sorbent in the display case, usually along with signage explaining the purpose of the white or black pellets. This is an excellent opportunity to educate the public about preservation issues and preventive conservation.

As discussed earlier, a combination of mitigation measures may be needed to satisfactorily reduce the concentrations of gases in a microenvironment or macroenvironment.

## Test, Test, and Retest

Mitigation efforts are best if supported by a three-part testing program. (1) Test prior to treatment to establish the baseline or before-treatment

## Table 6.1.

Selected sorbents used in conservation

Sorbent <sup>a</sup>	Uses	Drawbacks	
Carbon (activated charcoal), granulated activated carbon (GAC) Form: black pellets Gas Removal Process: adsorption	<ul> <li>A catchall sorbent that removes hydrocarbons, chlorine, nitrogen oxides (especially NO<sub>2</sub>, not as effective at removing nitrogen monoxide), and VOCs. Recent research shows that carbon also removes organic carbonyl pollutants (Druzik 2001, 2003).</li> <li>Used in HVAC systems to filter gaseous pollutants.</li> </ul>	<ul> <li>Difficult to determine when exhausted and hence when to regenerate (by baking in high-temperature oven) or replace.</li> <li>In some countries, used carbon is classified as a hazardous waste material. Disposal is costly.</li> <li>In high humidity situations such as rain or fog, water vapor can replace organic compounds adsorbed within the pores of the carbon. These low-risk VOCs are released into the environment, which accounts for the odor frequently associated with rain events in facilities with carbon gas filtration media. However, in a microenvironment with temperature and relative humidity control, this should not be a problem.</li> </ul>	
		ped as large molecules. Hence, effec- tiveness increases with molecular weight of gas.	
Activated carbon and activated alumina impregnated with potassium hydroxide	• Used to remove hydrocarbons, VOCs, and $NO_2$ .	• Can only be regenerated as activated carbon without impregnated chemical.	
Form: irregular pellets			
Gas Removal Process: chemisorption			
Activated charcoal cloth or carbon cloth (Zorflex®) <sup>b</sup> Form: cloth or paper impreg- nated with activated carbon Gas Removal Process: adsorption	<ul> <li>Useful in microenvironments with low-level emissions starting with low concentrations of pollutants; eliminates same gases as activated charcoal.</li> <li>Good mitigation treatment for display cases and storage cabinets.</li> </ul>	<ul> <li>Small reserve of carbon to adsorb pollutants. Cannot expect longevity.</li> <li>Should be replaced frequently.</li> <li>Cannot be regenerated.</li> </ul>	
	• Easy to use. Apply between base and object, e.g., under fabric liner.		
Activated alumina impregnated with potassium permanganate Form: purple spherical pellets Gas Removal Process: chemisorption <sup>c</sup>	<ul> <li>Highly reactive, strong oxidant. Removes nitrogen monoxide, aldehydes, sulfur oxides, and other odorous gases such as hydrogen sulfide. Also targets amines, mercaptans, and organic acids.</li> <li>Fresh material is purple; spent (exhausted) pellets are brown. This is a useful indicator that the sorbent should be replaced.</li> </ul>	<ul> <li>Potassium permanganate is caustic. Use precautions when handling,<sup>d</sup> and avoid contact with objects.</li> <li>Quickly exhausted. Must be replaced frequently, adding to cost.</li> <li>Water vapor will decrease reactivity.</li> <li>Cannot be regenerated; must dispose of as hazardous waste.</li> </ul>	
Zinc oxide catalyst G 72-D Form: cylindrical white pellets Gas Removal Process: chemisorption	<ul> <li>Removes reduced sulfur gases, e.g., hydrogen sulfide.</li> <li>Higher affinity for hydrogen sulfide than either activated carbon or alumina impregnated with potassium permanganate.</li> </ul>	• Cannot be regenerated.	
	• Easy to use. Place a few pellets in a Petri dish in a microenvironment.		
	<ul> <li>Used by the British Museum to protect silver and other susceptible objects.</li> </ul>		

#### Table 6.1 (continued)

Sorbent <sup>a</sup>	Uses	Drawbacks
Modified zinc oxide (Miracle Sac) <sup>e</sup> Form: solid granules in porous bags similar to tea bags	• Removes hydrogen sulfide, carbonyl sulfide, and mercaptans, which cause tarnishing.	• Cannot be regenerated.
Gas Removal Process: chemisorption		
Treated silver cloth – similar to bags sold commercially to pro- tect silver (Pacific Silvercloth®) <sup>f</sup>	<ul> <li>Acts as a sacrificial surface to rapidly remove reduced sulfides before they can reach silver objects</li> </ul>	<ul> <li>Limited lifetime, although the cloth can be effective for several decades, depending on the environment where</li> </ul>
Form: cotton or polyester felted acrylic cloth impregnated with finely ground silver	• Cloth can be glued to drawers or cabinet walls or ordered as bags to hold silver objects.	<ul><li>Cannot be regenerated.</li></ul>
Gas Removal Process: chemisorption		
	Selected Media That May Be Useful in Conservation	
Activated carbon impregnated with potassium iodide	<ul> <li>Used to remove hydrogen sulfide and prevent generation of sulfuric acid in microenvironments.</li> </ul>	• Can only be regenerated as activated carbon without impregnated chemical.
Form: irregular pellets		
Gas Removal Process: chemisorption		
Activated carbon impregnated with iron oxide	<ul> <li>Used to trap and oxidize gaseous pollutants such as hydrogen sulfide.</li> </ul>	• Elemental sulfur is a byproduct and can react in air to form sulfuric acid, which is
Form: irregular pellets		damaging.
Gas Removal Process: chemisorption		• Can only be regenerated as activated carbon without impregnated chemical.
Source: Information in this table was compiled fro (http://www.cwaller.de/sorbents.htm) as well as of	om Conservation OnLine (http://palimpsest.stanford.edu), Purafil® Inc. (http her websites listed. producte	p://www.Purafil.com), C. Waller's Long Life for Art site

Trade names are listed for specific conservation products.

<sup>b</sup> Available from Calgon Carbon Corporation (http://www.calgoncarbon.com) and Charcoal Cloth International, U.K.

<sup>c</sup> An irreversible reaction occurs between the media's active ingredient and the gaseous pollutant.

<sup>d</sup> The pellets and the powder from the pellets are irritating to the eyes and respiratory system. Review Material Safety Data Sheets before handling.

<sup>e</sup> Available through Long Life for Art: http://www.cwaller.de/sorbents.htm.

<sup>f</sup> Preservation Equipment Ltd. (http://www.preservationequipment.co.uk). Available from Nancy's Silver Shop (Fallbrook, Calif.; http://www.nancysilver.com); Art & Books (San Francisco, Calif.; http://www.art-books.com); Gaylord Bros. Library/Archive Suppliers (Syracuse, N.Y.; http://www.gaylord.com); and others.

pollutant levels. If mitigation is done soon after a problem is detected, the test results that identified the problem can be used to establish a baseline. If mitigation is done more than three to six months later, test again to get a current baseline reading. (2) Test within three months after mitigation to evaluate its effectiveness. (3) Retest the environment after enough time has elapsed for it to stabilize, typically six months to a year. Micro-environments must be left undisturbed for at least a month prior to any testing, so that gas concentrations are at an equilibrium.

#### **Preventive Conservation**

Museums can greatly reduce the pollutant risk to collections by practicing *preventive conservation*. This global approach to conservation encompasses much more than selecting the proper building and display materials to reduce gaseous pollutants. It also includes the formulation and implementation of museum policies and procedures for the correct handling and maintenance of objects for storage, exhibition, packing, housekeeping, transport, use, and display, as well as the production of facsimiles for the purpose of preserving an original object. Preventive conservation extends to integrated pest management and emergency preparedness and response.

Preventive conservation is the ideal for which museums should strive, although, realistically, putting into practice all of its tenets may be difficult for many museums. For pollution control, for example, preventive conservation assumes that museums have the luxury of sufficient resources—fiscal, time, and staff—to conduct the appropriate battery of preconstruction tests for all materials that will be used in proximity to objects over both the short term and the long term. And even when preventive conservation is the goal at the outset of new construction, something can easily be overlooked, as occurred at Scotland's Burrell Collection (see sidebar "Monitoring in Action: Burrell Collection").

Promoting preventive conservation has been a major objective of the GCI. From 1990 to 1995, the GCI offered an annual course titled "Preventive Conservation: Museum Collections and Their Environment." Instead of individual courses, the GCI has developed a website, "Conservation Teaching Resource," with a variety of resources including materials developed for its courses and workshops as well as new materials.<sup>6</sup>

The Canadian Conservation Institute has developed the exhaustive Framework for Preservation of Museum Collections that outlines various methods that can be used to avoid or control potential deterioration to museum objects. This framework, presented in a matrix format, is available online (www.cci-icc.gc.ca) and as a laminated wall chart that can be purchased from the Canadian Conservation Institute's bookstore.

Within each class of threat, the framework offers a five-step counterapproach: (1) Avoid; (2) Block; (3) Detect; (4) Respond; (5) Recover/Treat. The first four steps are part of preventive conservation. When these steps are not possible or fail, then the last step comes into play and involves the repair, conservation, and restoration of the damaged object.

The following expands on the framework's five steps for countering pollutants in museum environments:

- 1. Do not use materials that threaten the collection.
- 2. If you must use inferior materials, block emissions from reaching the objects.
- 3. Survey the collection regularly to detect early signs of deterioration and monitor air quality for potentially dangerous pollutants when

# Monitoring in Action: Burrell Collection

In the early 1980s, Glasgow Museums in Glasgow, Scotland, built a new museum to display the treasures that Sir William Burrell and his wife, Constance, Lady Burrell, had gifted to the city. The museum, named the Burrell Collection, was located in Pollok Country Park away from downtown at the city's limits. Part of the reason for choosing this site was to avoid the damaging effects of urban air pollution.

The museum and display cases are constructed of metal, stone, and glass that create a glorious background for the displayed collections. The museum was specifically designed with these materials to protect the objects from damage by gaseous pollutants that might be released by other types of building products. The storage areas, however, were a different story.

An odor indicative of wood and wood products greeted staff entering the storage vault. The odor came from the storage cabinets that had been constructed with a variety of materials, from medium-density fiberboard to improper adhesives that off-gas potentially damaging organic carbonyl pollutants. At the Burrell Collection, all of the planning to protect the collections from pollutants went into the design of the museum and its display cases, but not into its stores. This was an oversight with damaging consequences.

The first signs of trouble appeared a few years after the museum opened, when the conservators noticed discolorations or corrosion on objects in storage. The lead joins of prized stained glass panels housed in these inferior cabinets had corroded from the reaction of organic carbonyl pollutants with the lead (see chap. 2, fig. 2.4). An Egyptian seated goddess in bronze (see chap. 2, fig. 2.2) developed a blue corrosion product on its shoulder that was identified as an efflorescence of sodium copper acetate carbonate (Thickett, Bradley and Lee 1998). A twentieth-century replica of an Egyptian limestone relief (see chap. 2, figs. 2.7a, 2.7b) had developed a peculiar efflorescence identified as calcium acetate chloride nitrate (Gibson et al. 1997a, 1997b). This unusual corrosion product was named thecotrichite, which Tennent and colleagues (1995) claimed was derived from a Latin name meaning "hairy mineral from a storage cabinet." Burrell Collection officials donated this object to the conservation scientists at the Glasgow Museums so that its corrosion products could be studied further.

Alerted by the conservators, conservation scientists immediately took steps to identify the cause of the damage and to remedy the situation. Air quality monitoring detected the four organic carbonyl pollutants in the storage cabinets, but only the acetic acid reacted with the limestone<sup>1</sup> and the Egyptian bronzes. It was unclear which pollutant was reacting with the lead in the stainedglass joins; the corrosion products could be both acetates and formates.

Air quality monitoring also revealed that concentrations of the organic carbonyl pollutants were higher in cabinet recesses where air could not circulate, whether the cabinet was open or closed (Gryzwacz and Tennent 1994). This demonstrated the importance of air circulation in disbursing and diluting pollutants. Furthermore, though the cabinets were at least ten years old, they emitted significant levels of pollutants.

To mitigate this dangerous storage situation, the museum removed the problematic wooden cabinets (keeping one for study purposes) and replaced them with metal, open-grid racks. These racks secured the objects from theft, yet allowed air circulation to prevent accumulation of dangerous pollutants that might come from the objects themselves.

<sup>1</sup> This is not like Byne's Disease (or Byne's Efflorescence), which is a complex mixture of calcium acetate and calcium acetate formate salts. The occurrence of Byne's Disease in land shells, seashells, and other calcareous objects is dependent on the concentration of formalde-hyde and acetic acid, as well as on factors such as temperature and relative humidity.

warranted. This is a fundamentally important step, although it is often unfeasible in this era of decreasing human resources and collections that number in the millions of objects.

4. If a pollution threat has been detected, palliative measures are necessary. Either reduce the pollution levels with mitigation methods or relocate the objects to a "clean" environment. As described above, test, test, and retest should be the rule for effective mitigation. 5. If extensive damage has already occurred, conservation of the objects may be necessary. At the same time, the environmental conditions must be improved to prevent continued deterioration.

## Conclusion

Creating a pristine museum environment for collections is impossible. We do not fully understand how gaseous pollutants damage collections. Furthermore, the limited funds and time available to museums affect their ability to implement pollution prevention and abatement measures. However, limited resources and gaps in knowledge should not deter museums from protecting their collections and archives. As this book shows, enough information is available to help museums make even modest environmental improvements. Tomorrow may bring to light better materials and methods for pollution control, but objects are deteriorating today, and action must be taken.

Above all, minimizing the adverse effects of gaseous pollutants on collections begins with awareness of the museum environment. In "The Pollutant Problem in Perspective," Bradley and Thickett (1999b:22) wrote, "The most important thing we do has not changed in the 245 years since the [British] Museum was founded, it is to look at the objects."

#### Notes

- 1. An irreversible reaction occurs between the media's active ingredient and the gaseous pollutant.
- 2. Interestingly, at the first sampling at one week, the highest concentration of acetic acid was detected not in the control display case, as was expected, but in the display case with the barrier foil and chemically treated build-ups. This is a good example of encountering a monitoring result that does not make sense. A review of the experiment's documentation showed that for this display case, its acrylic vitrine had been placed on the wood base too soon after it was cleaned with a solution containing acetic acid, e.g., solution of vinegar, trapping the gas inside the display case. A replacement was built and tested.
- 3. The latter is available online at http://iaq.dk/papers/good-bad-ugly.htm.
- 4. Medex<sup>®</sup> and Medite II<sup>®</sup> (Sierra Pine Ltd., http://www.sierrapine.com) are wood composite boards that use a formaldehyde-free synthetic resin; there are no formaldehyde emissions. These products should not be confused with Medite MDF<sup>®</sup> and Medite FR2<sup>®</sup>, which are bound with a urea formaldehyde-based binder and do emit formaldehyde.
- 5. This poses a particular problem for certain highly reactive gases, such as reduced sulfides (i.e., hydrogen sulfide and carbonyl sulfide) that rapidly tarnish silver surfaces. Not many sorbents can compete with silver's affinity for sulfides, but a few are listed in table 6.1. For example, the British Museum has had success with a modified zinc oxide pellet (Baird et al. 1992; Casarin 1995).
- 6. The GCI websites are as follows: GCI Conservation Teaching Resource, http://extranet.getty.edu/gci/teaching/; Teaching Materials for Preventive Conservation, http://extranet.getty.edu/gci/teaching/preventive.

## The J. Paul Getty Museum Monitoring Program, 1996-1998

The J. Paul Getty Trust began planning for the Getty Center in the early 1980s. It purchased eighty acres atop a hill at the northwestern edge of the Los Angeles basin. This would be the future home of the various operating programs within the J. Paul Getty Trust. The pinnacle of the campus would be the J. Paul Getty Museum (fig. 7.1).

Because much of the museum's collections would be on open display and not in showcases, providing the cleanest indoor environment possible was a primary concern. To that end, significant financial and staff resources were dedicated to a clean air effort that began in the planning stages. All precautions to minimize, if not eliminate, the risk of damage to objects due to air pollution were implemented. An exceptional HVAC system was designed to remove outdoor pollutants from the air before they entered the museum's galleries and storage areas.<sup>1</sup> In addition, more than eight hundred construction and design materials to be used in galleries and display cases were first tested by the GCI Museum Research Laboratory using multiple tests. If samples off-gassed harmful vapors, the materials were not approved for use in the museum, especially in microenvironments.<sup>2</sup>



**Figure 7.1.** View of the J. Paul Getty Museum. Photo: Tom Bonner © J. Paul Getty Trust

Were these preemptive efforts effective? Did the thorough pretesting of materials guarantee a clean environment, free of indoorgenerated pollutants? Was the HVAC system removing outdoorgenerated pollutants and delivering clean air throughout the museum?

Fortunately, we had the opportunity to evaluate this effort by conducting an intensive two-year air quality monitoring program that spanned the museum's construction phase through its opening. This was the first time that such thorough air quality monitoring data of a new museum had been compiled.

### The Museum Monitoring Program

Testing for pollutants began in August 1996 while the museum was still under construction, because galleries with wall panels had to be installed at the same time. Air quality monitoring continued through the opening of the J. Paul Getty Museum at the Getty Center on December 16, 1997, and for the first few months afterward to determine the impact of visitors on air quality. The five phases of museum construction and relevant air quality monitoring activities are listed in table 7.1. This fivephase program would provide important off-gassing levels and emission decay rates for pollutants as well as data on the effectiveness of the HVAC system.

### **Monitoring Locations**

Four monitoring locations were selected. Intakes for two main air handling units (AHUs) of the HVAC system were monitored: one facing east toward the San Diego Freeway (Highway 405) and the other west toward the ocean, to see if the ambient air would be cleaner coming from the ocean than from the direction of the freeway. In addition, a gallery served by each AHU was monitored: the Rococo Gallery on the Plaza level for the east AHU and the Italian Paintings Gallery<sup>3</sup> on level 2 for the west AHU.

The east air handling unit was the first to go online, expedited by the installation of the Rococo Gallery's wall panels. When the rest of the museum's HVAC system was turned on three and a half months later, monitoring in the Italian Paintings Gallery began.

Although the collections in the museum are primarily on open display, a number of objects are housed in display cases. At the request of the Decorative Arts and Sculpture Conservation Department, we tested four Kunstkammer cases constructed of aluminum and glass for possible off-gassing from adhesives or gaskets and two wall cases constructed only of materials that had been approved by the GCI Museum Research Laboratory after materials testing. We did not expect to detect any gases, but we wanted to be sure that there were no emissions present.

At the request of the Manuscripts Department, we also evaluated two new display cases as well as a new book cradle design. The new cradle was enclosed in a display case for testing, as was an old cradle, which was tested for comparison.

## Table 7.1.

The five air quality monitoring phases and relevant construction activities for the J. Paul Getty Museum at the Getty Center

Time Frame	Construction Activities	Air Monitoring Activities
Phase I July 29– November 10, 1996	Exterior to the museum there was extensive construction traffic and landscaping work. HVAC system operating with 100% recirculating air, no	Gas and particle samplers were placed before the intake fan of the East air handling unit, the first to go online. Indoor samplers were placed in the Rococo Gallery and Regence Gallery.
	heavy construction continued in the museum. Contractors worked continuously. Building shell had not yet been sealed, creating many openings to outdoor air. A lot of dust and a high particle load were present. But the air was cleaned significantly over the weekend as it recirculated through the HVAC system.	The West location was outdoors, not in an air handler. The first two sampling periods were not successful because the samplers were exposed and got wet from work by the grounds department. A shelter was built to protect the samplers from water, including rain.
Phase II November 10– March 27, 1997	Because of the heavy construction work, a coarse-particle screen was placed in front of the intake to the East air handling unit for three months. The intake fans were operational, and the HVAC system outdoor air supply was turned on. Heavy construction activity continued; however, the building shell was completed and sealed.	It was the start of the 1997–1998 El Niño event, <sup>1</sup> which produced substantial amounts of rainfall. Concentrations of outdoor gases were generally low during this winter period, except for high readings at the East air intake due to major highway and construction traffic near this location.
	During this period, there was a lot more extensive, dirty work going on in the galleries: painting, gilding, laying	Monitoring shifted from the Regence Gallery to the Italian Paintings Gallery.
	noors, and general infishing touches.	The West site was still an outdoor shelter.
Phase III March 10– June 25, 1997	Construction was completed, and the galleries were turned over to the J. Paul Getty Museum at the Getty Center on March 10. Art installation began and contin- ued through the end of May. With the work on the museum completed, construction	Samplers in the East air handling unit got very dirty. The West outdoor location was moved inside an air handling unit with a west-facing air intake. The samplers were located after the intake fan and did not get as dirty. The Rococo Gallery and Italian Paintings Gallery were moni-
	outside moved to the west side of the site, where the Getty Research Institute was being built.	During this phase and the next, higher levels of outdoor pollutants were detected in the West air intake, which was directly related to construction of the Getty Research Institute to the west of the museum.
Phase IV May 27–	Art installation was completed. The museum was still closed to the public, and staff access was controlled.	Phase IV was the control period—after most of the art installation and before the public opening. Differences in air quality were measured and could be attributed to various activities in preparation for the opening in December.
December 6, 1997	Construction continued outside, in particular, work on the Getty Research Institute to the west of the museum.	
Phase V November 10,	During November, the final opening preparations were completed.	Monitoring for gaseous pollutants continued as normal throughout this period.
1997–May 15, 1998	There was a great deal of planting and repotting of plants prior to the opening.	Particle samples were not collected during special events because of the pump noise. Once the museum opened,
	Numerous visitors came to the museum for the many preopening events and for the Grand Opening on December 16, 1997. Through early January, daily visitor attendance was excessive. The average daily attendance was 9,400 and reached as high as 16,500. The average daily attendance from mid-January through April dropped to 5,730 (Drolet 2005).	particle measurements were obtained only on Closed Mondays. In February, especially quiet pumps arrived and tests continued on days when the museum was open to the public.
		Data collected during this phase confirmed the ability of the HVAC system to maintain ultra low levels of pollu- tants despite record numbers of visitors. People bring in particles and VOCs and allow infiltration of outdoor-gen- erated pollutants when entering and leaving the building.
		The winter rains of El Niño were very heavy. Los Angeles had the wettest winter and the fourth wettest spring on record (1944–2005) (NCDC 2005). This contributed to the low outdoor concentrations of pollutants.
<sup>1</sup> El Niño (Spanish for Ecuador and Peru and spheric consequences WW2010 <sup>TM</sup> 2005).	"male child") is a warm current of water. The term initially referred to a weak, war lasting only a few weeks to a month or more. Every three to seven years, an El Niñ worldwide. During the past forty years, ten of these major events have been record	m current appearing annually around Christmas time along the coast of io event may last for many months, having significant economic and atmo- led, the worst of which occurred in 1997–98 (Weather World 2010 Project

#### Passive sampling devices

Passive sampling devices were chosen for the monitoring program because they are simple to use and do not require sophisticated technology or extensive fiscal and staff resources. A variety of commercial and noncommercial samplers were selected to provide data on the intercomparison of devices.

The devices and the gases they monitored are listed in table 7.2. For ease of use and deployment in the macroenvironments (the air handling units and galleries), the sampling devices were mounted on 20 cm<sup>2</sup> Plexiglas panels (fig. 7.2), except for the Purafil<sup>®</sup> Environmental Reactivity Coupons, which were attached separately at the monitoring locations using Velcro.

At the east AHU, the gas samplers were placed approximately a meter high inside the air intake but before the fan and all filters. At the west AHU, the samplers were placed after the intake fan but before the filters.

In the galleries during the initial phases of construction, there were few restrictions on the PSD panel locations. After the collections were installed, the samplers were hidden from view for aesthetic reasons: behind a corner screen in the Rococo Gallery (fig. 7.3) and secured with Velcro to the back of a large pedestal in the Italian Paintings Gallery.

Each month new sets of samplers were deployed, and the previous month's PSDs were retrieved and sent out for analysis.

In the display cases being tested, the samplers were set out on a shelf. For the book cradles, they were placed where a manuscript would rest (see chap. 5, fig. 5.7). The microenvironments were only tested once or twice, independently of the construction phases.



#### Figure 7.2

Assorted PSDs mounted on a Plexiglas panel facilitated deployment. The panel is propped up for the photograph. Each pack of Oxford Brookes University Open-Path Diffusion Tubes contains the same five samplers: nitrogen dioxide, hydrogen sulfide, ozone, organic acids, and sulfur dioxide. Photo: Cecily M. Grzywacz © J. Paul Getty Trust

## Table 7.2.

Passive sampling devices used in the J. Paul Getty Museum Monitoring Project

Pollutants Detected	Sampler Type	Comments
Formaldehyde	GMD Formaldehyde Dosimeter	GMD Formaldehyde Dosimeter badges were purchased from Scott Instruments, Exton, Pa. Initially, the badges were analyzed at the manufacturer's lab. Later, the badges were analyzed at the GCI Air Pollution Analysis Laboratory using the GCI-developed protocol in Appendix 4.
Nitrogen dioxide, sulfur dioxide, ozone, organic acids, hydrogen sulfide	Oxford Brookes University Open-Path Diffusion Tube	Open-path (Palmes) diffusion tubes were supplied by the Biogeochemistry Research Group at Oxford Brookes University in Oxford, England. Immediately after exposure, the tubes were returned to the university by express mail for analysis; the results were reported by e-mail.
		<i>Note:</i> Hydrogen sulfide, a major risk to collections at very low concentrations, has to be quantified at the parts per trillion level. This is extremely difficult. Only Oxford Brookes University provides a diffusion tube sampler that detects ppt of hydrogen sulfide. The cost was £200/ $\cong$ \$325 (1996–98) for each location. The potential threat of this gas warranted the expense.
Nitrogen dioxide, sulfur dioxide, ozone	Ogawa Passive Samplers	These badge-type samplers were purchased from Ogawa & Co., USA, Inc., Pompano Beach, Fla. After exposure, the samplers were returned by overnight delivery to Ogawa for analysis.
Total VOCs	3M Air Monitors	The 3M monitors were purchased from Lab Safety Supply, Inc., in Janesville, Wis. After exposure, they were returned to the independent laboratory indicated by the company with the postage-paid envelope provided.
Corrosive gases	Purafil <sup>®</sup> Environmental Reactivity Coupons	Purafil supplied Environmental Reactivity Coupons. After exposure, they were returned to Purafil for analysis.

## Target gaseous pollutants

The Science Department of the GCI conducted the evaluation of gaseous pollutants in the museum.<sup>4</sup> The museum was monitored for the following pollutants:

• sulfur dioxide (SO<sub>2</sub>), a primary outdoor pollutant from the combustion of coal and other fossil fuels. Although SO<sub>2</sub> is not a significant pollutant in Los Angeles, it was included



## Figure 7.3.

Decorative screen in a corner of the Rococo Gallery hides pollutant monitoring equipment. Photo: Jack Ross © J. Paul Getty Trust to determine if the diesel equipment increased the concentrations locally at the Getty construction site and especially to ensure that if elevated levels were generated, they did not infiltrate the museum.

- nitrogen dioxide (NO<sub>2</sub>), a major outdoor photochemical smog component from vehicular pollution
- ozone (O<sub>3</sub>), a secondary vehicular pollutant generated by the reaction of nitrogen oxides and hydrocarbons with oxygen and light
- hydrogen sulfide (H<sub>2</sub>S), which can be generated outdoors from natural sources and industrial processes, as well as indoors by off-gassing from construction materials
- organic carbonyl pollutants (formaldehyde and organic acids), which are normally associated with indoor pollution but are increasing outdoors due to the use of alcohol-based fuels
- total VOCs, an overall measure of indoor air quality
- corrosive gases in general.

These pollutants were selected because of the Getty Center's location in the Los Angeles basin, and its superb hilltop views usually include an orange-brown smog layer. The Getty Center sits above one of the busiest sections of the busiest freeways in the country, the Sepulveda Pass of the San Diego Freeway.

## Monitoring results: Macroenvironment

Unfortunately, Grzywacz, Donohoe, and Villalta (2001) found that readings from the Oxford Brookes University open-path diffusion tubes that were placed inside the AHU air intakes were not accurate, and their readings of the outdoor air quality were not included in the results. Inside the air intakes, these devices were subjected to extremely high air velocities when the intake fans were on. High air velocities and turbulence effectively reduce the diffusion path length, resulting in artificially high readings (Watts and Ridge 1999). (See chap. 4, sidebar "Consideration for Using Open-Path (Palmes) Diffusion Tubes"). Despite this location bias, the Oxford Brookes samplers in the AHUs recorded low outdoor concentrations of H<sub>2</sub>S and organic acids. Fortunately, the Ogawa PSDs are not as sensitive to high air velocity, and we were able to use the Ogawa data for SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub>. We could confirm the validity of these concentrations because there was another outdoor air quality testing project at the Getty Center.<sup>5</sup> In addition, the South Coast Air Quality Monitoring District's (SCAQMD) Northwest Coastal Regional test station was located within a couple of kilometers of the Getty Center. The concentrations measured at the museum's AHUs, at the United Nations testing station at the Getty Center, and at the SCAQMD site were in good agreement.

Outdoor-generated pollutants:  $NO_2$ ,  $O_3$ , and  $SO_2$ . The coastal area in which the museum is located historically has had low concentrations of pollutants due to dilution with the ocean air (SCAQMD 2002).

We expected moderate to low concentrations of these outdoor-generated pollutants, with the lowest levels at the ocean-facing west air intake. We did record low concentrations, but the westerly levels of nitrogen dioxide and ozone were not always lower than concentrations measured at the freeway-facing east air intake. This was attributed primarily to construction. When machinery traffic was near the east air intake, the pollutant concentrations were greater there than at the west air intake. However, once work on the museum was completed and construction efforts intensified at the Getty Research Institute to the west of the museum, higher pollutant levels were detected at the west air intake. Diurnal onshore and offshore wind currents also could have contributed to the variations in concentrations.

Because Southern California uses low-sulfur fossil fuels and therefore does not have  $SO_2$  pollution, the extremely low sulfur dioxide levels—frequently less than the Ogawa PSD detection limits (0.2 ppb)—were expected.

Infiltration of outdoor pollutants. Indoor/outdoor ratios were calculated for the target outdoor-generated gases (NO<sub>2</sub>, O<sub>3</sub>, and SO<sub>2</sub>) to measure the effectiveness of the building's HVAC system to prevent penetration of outdoor gases. Once the building was completed, the I/O ratios of nitrogen dioxide were less than 0.06; that is, the NO<sub>2</sub> concentrations in the galleries were 6 percent or less than the outdoor concentrations (see fig. 7.4). This indicated that the building and the HVAC system were effectively keeping this pollutant out of the museum.

I/O ratios of ozone were zero because it was not detected in the galleries over the monitoring period, except during Phase 2 of construction, and even then, it was only 1 ppb (see fig. 7.5). As mentioned in chapter 5, ozone is reactive and unstable and will be reduced by standard HVAC systems, even without gaseous filtration.



#### Figure 7.4.

During Phase I, the building shell was still open to the outdoor air as construction work continued. The concentration of nitrogen dioxide detected in the galleries was nearly half the levels observed outdoors. In Phase II, concentrations increased outdoors, but there were lower levels inside, a direct reflection of the sealing of the building. Once construction inside the building was completed and the building was handed over to the museum, the concentrations in the galleries decreased significantly. This dramatically demonstrated the effectiveness of the HVAC system to remove outdoor-generated pollutants. In the first two phases, the concentrations were greater on the east side of the property. Once construction of the Getty Center Museum was completed, construction intensified to the west of the museum to complete the Getty Research Institute. This is reflected in the higher outdoor concentrations seen at the West air intake.



Because sulfur dioxide was not detected outdoors or indoors, I/O ratios were not relevant for this gas. It is not a threat to the Getty's collections.

*Indoor-generated pollutants.* The indoor levels of hydrogen sulfide were at or below the PSD's detection limits (15–60 ppt).

Concentrations of the organic carbonyl pollutants (organic acids and formaldehyde) were low in the galleries, except during Phase V when the museum was opened to the public. Formaldehyde levels in the Italian Paintings Gallery doubled with the influx of thousands of visitors. Organic acids concentrations also increased because of the number of people in the museum. However, the organic carbonyl pollutant levels (8–30 ppb) did not pose a risk to the collections.

*Total VOCs.* The concentration of total VOCs, a good indicator of general indoor air quality, dropped dramatically once construction was finished. Figure 7.6 shows how the total VOCs level in the two monitored galleries increased slightly with the influx of people during preopening events, the grand opening, and especially after the museum was officially opened to the public. Attendance was extraordinary, in the tens of thousands of visitors, during the first few months after the museum opened. Hence, this initial increase in pollutants did not reflect the true impact of visitors. Once attendance leveled off, concentrations of total VOCs decreased and have consistently remained below the maximum level considered acceptable for total VOCs. These results illustrate that with the use of proper construction materials, preservation-friendly products (i.e., products that do not emit harmful gases), and an HVAC system with gaseous filtration, high levels of VOCs are avoidable in new museums.

*Corrosive gases in general.* Based on results from silver and copper Environmental Reactivity Coupons, which were deployed for the first six months of the monitoring program (Phase I and part of Phase II), the environment in the galleries being tested was rated "ISA Class G1 Mild"; that is, corrosion was not expected.

Ozone was detected in the galleries only during Phase II, and this was a very low level, 1 ppb. Throughout the rest of the project, ozone was not detected in the galleries. In every phase, higher concentrations of ozone were detected in the air intake on the west side of the property than on the east side of the property. Total VOCs Detected at the J. Paul Getty Museum at the Getty Center, 1996–1998

#### Figure 7.6.

High concentrations of total VOCs in the two galleries being monitored were observed during the construction phases (I and II) of the museum. The slightly higher readings during Phase II reflect increased workloads to complete the museum on time. The levels dropped dramatically when the building was completed (Phases III and IV) and the major activities were art installation. Although still very low, total VOCs increased slightly when the museum opened to the public (Phase V), reflecting daily attendance, which frequently exceeded six thousand visitors during the first five months, and museum cleaning.



#### Monitoring results: Microenvironment

In the display cases tested for the Decorative Arts and Sculpture Conservation Department, concentrations of all organic carbonyl pollutants were low, and no hydrogen sulfide was detected. Similar results were obtained from the display cases tested for the Manuscripts Department. These results affirmed the tremendous effort put into pretesting every material used to build the enclosures.

A very low amount of hydrogen sulfide was detected in the display case holding the old book cradle, but this was not a concern because it was at the detection limit. However, moderate levels of hydrogen sulfide (130 ppt) were detected in the case holding the new book cradle design. This level was not acceptable because of the risk to silver gilt used on illuminated manuscripts. The cradles were redesigned and cured for a longer time in a fume hood. Subsequent testing confirmed that they no longer posed a risk from  $H_2S$  emissions.

## Summary

The results of the museum monitoring program underscore the success of planning, design, and testing efforts aimed at maximizing indoor air quality. The results also demonstrate the usefulness of passive sampling devices for monitoring both macroenvironments (galleries) and microenvironments (display cases).

Because of the design of the outstanding HVAC system and prior testing of every construction material, indoor air quality was extremely good. The air inside the building was very clean, even on smoggy days. The exception was the high levels of total VOCs during

construction Phases I and II when work activities and the products being used released VOCs. But once the museum was completed, the level of total VOCs dropped significantly. Until this study, it was assumed that all buildings required an off-gassing period before art was installed.

The J. Paul Getty Museum at the Getty Center's success was the result of an extraordinary collaboration among conservators, designers, engineers, and scientists. This collaboration continues and has made it possible to quickly resolve any ensuing air quality issues.

#### Notes

1. The museum's HVAC system is a dual-system: "Outside Air-Handling Units" distribute air to "Museum Air-Handling Units." Fresh air is conditioned by each air handling unit (AHU) type to collections specifications, 52% RH  $\pm 2\%$  RH and  $70°F \pm 2°F$  ( $21°C \pm 1°C$ ). There are 11 gallery fan systems and 7 outside air fans systems that serve the collection areas of the museum. The museum AHUs run 24 hours a day, 7 days a week.

The museum AHUs or fan systems consist of two parallel fans with a complete set of filters (prefilters, 65%; carbon filters, virgin coconut carbon, 60 CTC, 4 x 8 screened, and final filters, 95%), cooling coils, and steam humidification. The fans are equipped with vortex dampers, which modulate. When both fans are running in parallel, they are about 60% open. If one fan fails, the other automatically ramps up to 100% and the constant volume boxes on the system reduce to 60% of their volume to provide even air distribution throughout the museum's collection areas. The humidification is controlled by return air (52% RH), and the discharge temperature of the fan is set to 11°C (52°F), which provides 21°C  $\pm$  1°C and 52% RH  $\pm$  2% RH air to galleries, storage rooms, and other art collection rooms.

The museum fans receive outside air through a separate fan system that conditions and filters the air prior to being mixed with the return air form the galleries. These outside air units have prefilters, carbon filters, final filters, and humidification, which enables us to control the condition of the outside air year round. These units provide 20% to 25% outside air to the museum AHUs and hence the galleries (Donohoe 2005).

- Rabbit skin glue, which generates reduced sulfide gases, was the one exception. Because it was needed to gild panel walls in a gallery, the adhesive was approved for this limited use only. No airborne sulfides from the rabbit skin glue were detected during subsequent air quality monitoring at a detection limit of 15 ppt.
- 3. During Phase I of construction, the Regence Gallery was monitored, but for the remainder of the monitoring program monitoring was conducted in the Italian Paintings Gallery.
- 4. The museum monitoring program also included particulate monitoring, which was conducted by the California Institute of Technology in Pasadena, California. "Air Pollution in New Museum Facilities" (Salmon, Mayo, and Cass 1998) is the final report of this effort.
- 5. At the time of the monitoring program, the GCI was also participating in an international outdoor corrosion evaluation project for the United Nations. IVL diffusive samplers were used for this study (see chap. 4, table 4.5).

Appendix 1

Major Gaseous Pollutants of Concern to Museums, Their Sources, and At-Risk Materials
Gaseous Pollutants	Major Sources (and Some Minor Sources)	At-Risk Museum Materials
	Inorganic Pollutants	
Sulfur dioxide (SO <sub>2</sub> )	OUTDOOR SOURCES	<ul> <li>SO<sub>2</sub> can be absorbed onto cellulosic materials, such as</li> </ul>
$SO_2$ can react with water vapor in the air and form both $H_2SO_2$ and $H_2SO_2$ .	Natural Sources	paper, where it catalytically hydrolyzes to H <sub>2</sub> SO <sub>4</sub> . H <sub>2</sub> SO <sub>3</sub> and
Outdoors, in high humidity, the acidic gases coalesce into	Marine biological activity and active volcanoes.	H <sub>2</sub> SO <sub>4</sub> can also be absorbed directly onto these materials. The acid depolymerizes the cellulosic structure. Although
superfine, suspended droplets, or aerosols, known as acid rain. A similar reaction occurs indoors, where these acidic	Atmospheric reactions of hydrogen sulfide: $H_2S$ reacts rapidly with oxygen and forms both $SO_2$ and $H_2SO_4$ . <sup>1</sup>	the damage is invisible, affected materials are embrittled and weakened.
gases are deposited on surfaces and can cause damage.	Industrial Processes	<ul> <li>Sulfur dioxide and related acids react with animal skins, such as leather and parchment.<sup>14</sup> This breaks down the</li> </ul>
	The primary source of $SO_2$ is the combustion of sulfur- containing fossil fuels, including coal, gasoline, and diesel fuel. <sup>1</sup>	molecular structure and weakens the material. The surface becomes powdery and easily abraded, a condition referred to as "red rot." <sup>15</sup>
	Industrial processes associated with pulp and paper pro- duction, <sup>2</sup> cement industry, <sup>3</sup> and petroleum refineries, especially when less expensive, higher-sulfur-content	<ul> <li>Sulfur dioxide and its pollutant progeny react with acid- sensitive pigments. This usually results in a color change, which is typically nonreversible. For example, lead white is propriet to block producted contents in a doctored</li> </ul>
	Fireworks, which can be a localized, short-term risk <sup>4</sup>	converted to prack read surrace, resulting in a darkened color on the object where the white lead oxide is used. Lead-tin yellow, chrome yellow, verdigris, chrome orange,
	INDOOR SOURCES	emeraid green, and chrome red are some of the other pig- ments that are darkened by sulfates.
	Sulfur-containing fuels, such as kerosene and coal, that are used to cook and heat (relevant for historic houses as	<ul> <li>Fades dyestuffs, affecting the color of watercolors, tex- tiles, costumes, etc.<sup>13, 16, 17</sup></li> </ul>
	well as museums in areas that predominantly use these fuels) <sup>5, 6</sup> Firewood used to cook and heat. <sup>7</sup>	<ul> <li>Most metals, including copper, silver, bronze alloys, and aluminum, are susceptible to corrosion by any acidic species, causing irreversible damage.</li> </ul>
	Vulcanized rubber. <sup>8</sup> • Propane- or gasoline-powered machines, equipment, and generators. <sup>9</sup>	<ul> <li>Silver salts in photographs are attacked, darkening the image. Acidic sulfur gases break down gelatin, weaken photographic papers, and accelerate the deterioration of cellulose ester bases. Certain color dyes can be discolored.<sup>151</sup></li> </ul>
		<ul> <li>SO<sub>2</sub> attacks stone such as limestone, marble, dolomite, and other carbonate minerals or calcareous materials such as shells, clays, and tiles. At-risk objects include sculpture, natural history collections, and low-fire ceramics.</li> </ul>
		<ul> <li>When SO<sub>2</sub> is adsorbed on soot or carbon particles on dirty objects, it can be oxidized to sulfuric acid or sulfurous acid, a risk for all acid-sensitive materials.<sup>18</sup></li> </ul>

Note: Superscript numerals correspond to numbered references following the table.

Inogani Collection         Inorgani Collection         Inorgani Collection         Information         Information <th< th=""><th></th></th<>	
Ninose orda er da antide ad caracterization.         OUTDOOR SOURCES         Ninous acid and nific ad caracterization.         Ninous acid and nific ad caracterization.           VOX is a collective term for nitrogen monovide (NO) and nific add ar ar pollutant. It reacts with other chemical species in the art pollutant. It reacts with other demical species in the art pollutant. It reacts with other demical species in the art pollutant. It reacts with other demical species in the art pollutant. It reacts with other demical species in the pollutant and.         Ninous acid and nific add caracterization. and biomus shifter materials that are a start process such as sull microbe, vegetation, and biomass fire. Xinona cut. Xinona cut	
<ul> <li>Nox is a collective term for nitrogen monoxide (NO) and <i>Natural Sources</i> and <i></i></li></ul>	• Nitrous acid and nitric acid can damage the same acid-
<ul> <li>ar pollutari. It rectors with other chemical species in the number of the chemical species in the produce namy other rective with other chemical species in the produce namy other reactive intogen compounds. The color of photochemical smog.</li> <li>No, a purgent, red gas partly responsible for her color of photochemical smog.</li> <li>Agricultural fertilizers.<sup>4</sup></li> <li>Agricultural fertilizers.<sup>4</sup></li></ul>	sensitive materials that are attacked by sulfuric acid or sulfurous acid.
the color of photochemical smog.       Agricultural fertilizers. <sup>9</sup> <ul> <li>Agricultural fertilizers.<sup>9</sup></li> <li>Addation (ty ozone. UV irradiation, etc.) of nitrogen of fossil fuels for industry and vehicles is the privans date dyet.</li> <li>Advestifis and inter acid.</li> <li>Advestifis and intervents and outdoors. These acidic of moust and with urban traffic and thermal power phymeris in illuminated man are associated with urban traffic and thermal power phymeris in illuminated man are associated with urban traffic and thermal power phymeris in illuminated man are associated with urban traffic and thermal power phymeris in illuminated man are associated with urban traffic and thermal power phymeris in illuminated man are associated with urban traffic and thermal power phymeris in illuminated man are associated with urban traffic and thermal power and myon's causin travely are action of NO and NO<sub>2</sub> on interior protects including stass.<sup>11,2</sup> and with erabon and carbitrate corrode a gistic effect with H<sub>2</sub>.</li> <li>Affects the tranishing of cop plutants corrode and myon's causin there are acids, HNO<sub>2</sub> and the art and and carbitrates including stass.<sup>11,2</sup> and with erabon and carbitrate physic acids. Reactions in the acids, HNO<sub>2</sub> and the art and t</li></ul>	<ul> <li>NO<sub>2</sub> enhances the deterioration effects of SO<sub>2</sub> on leather, metals, stone, etc. <sup>29</sup></li> </ul>
Oxidiation (by ozone. UV irradiation, etc.) of nitrogen       Unrougen poluriants area over over trunces drapery, tapsetries, the solutions and outdoors. These acidic       Unrougen poluriants area over trunce, drapery, tapsetries, the primary source of introgen oxides. High concentrations primary source oxin primary source of introgen pollutants fade certications. Freworks are a temporary but relevant source.       Nitrogen pollutants fade certications primary source oxides. High concentrations primary source oxides. High concentrations primary source.         INDOOR SOURCES       Gas-Phase Reactions       Nitrogen pollutants corrode z splits effect with H <sub>2</sub> S.         Gas-Phase Reactions       Formation of codi cadis. Reaction of NO and NO <sub>2</sub> on interior sufface. Hou or and who acids. HNO <sub>2</sub> and HNO <sub>2</sub> , respectively.       Affects Harmishing of copi sufface. Here acids. HNO <sub>2</sub> and HNO <sub>2</sub> .         Indoor Activities       Stores, heaters, fireplaces, and other sources of combustion. <sup>3</sup> Affects here acids. HNO <sub>2</sub> and HNO <sub>2</sub> and HNO <sub>2</sub> and HNO <sub>2</sub> and HNO <sub>2</sub> .         Indoor Activities       Stores, heaters, fireplaces, and other sources of combustion. <sup>3</sup> Affects here acids. HNO <sub>2</sub> and HNO <sub>2</sub>	Corrosion of copper-rich silver.
The contribution of fossil fuels for industry and vehicles is the primary source of nitrogen oxides. High concentrations are associated with urban traffic and thermal power plants.	<ul> <li>Nitrogen pollutants rade ayed ribers in textiles, cos- tumes, drapery, tapestries, etc.<sup>13, 30</sup> Reactions with dyestuffs will alter the color of textiles.<sup>16, 17, 31, 32, 33</sup></li> </ul>
plants.       • Nitrogen pollutants degrade i sile, wool, and nylon, <sup>6</sup> causin         Fireworks are a temporary but relevant source. <sup>4</sup> • Nitrogen pollutants degrade i sile, wool, and nylon, <sup>6</sup> causin         INDOOR SOURCES       • Nitrogen pollutants corrode z gistic effect with H <sub>2</sub> .       • Nitrogen pollutants corrode z gistic effect with H <sub>2</sub> .         Gas-Phase Reactions       • Nitrogen pollutants corrode z gistic effect with H <sub>2</sub> .       • Affects the tarnishing of copt surfaces, including glass, <sup>21, 22</sup> and with carbon and carbon and carbon accous aerosols, <sup>23</sup> generates the acids, HNO <sub>2</sub> and HNO <sub>2</sub> and HNO <sub>2</sub> and HNO <sub>2</sub> and tarbon and carbon actor boncecous areosols, <sup>23</sup> generates the acids, HNO <sub>2</sub> and the sources of suffice. <sup>37</sup> • Affects the tarnishing of copt suffice. <sup>37</sup> Indoor Activities       • Indoor Activities       • Affects the acids, HNO <sub>2</sub> and the sources of suffice. <sup>37</sup> • Affects the tarnishing of copt suffice. <sup>37</sup> Indoor Activities       • Indoor Activities       • Affects the acids, HNO <sub>2</sub> and the sources of combustion. <sup>5</sup> • Affects and other sources of suffice. <sup>37</sup> Dispace sincles . <sup>24, 25</sup> Dry-process photocopiers. <sup>26</sup> Dry-process photocopiers. <sup>26</sup>	<ul> <li>Nitrogen pollutants fade certain inks as well as organic pigments in illuminated manuscripts.<sup>34</sup></li> </ul>
INDOOR SOURCES       • Nitrogen pollutants corrode z gistic effect with H <sub>2</sub> S. <i>Gas-Phase Reactions</i> • Affects the tarnishing of copp surfaces, including glass, <sup>21,22</sup> and with carbon and carbon excessions, <sup>23</sup> generates the acids, HNO <sub>2</sub> and With carbon and carb	<ul> <li>Nitrogen pollutants degrade fibers made from rayon, silk, wool, and nylon,<sup>6</sup> causing yellowing and embrittlement.</li> </ul>
Gas-Phase Reactions       • Affects the tarnishing of copy         Formation of acids: Reaction of NO and NO <sub>2</sub> on interior       • Affects the tarnishing of copy         Surfaces, including glass, 2 <sup>1, 22</sup> and with carbon and and and and and and and and and an	<ul> <li>Nitrogen pollutants corrode zinc;<sup>35, 36</sup> there is a syner- gistic effect with H<sub>2</sub>S.</li> </ul>
Formation of acids: Reaction of NO and NO, on interior surfaces, including glass, <sup>21, 22</sup> and with carbon and car- bonaceous aerosols, <sup>23</sup> generates the acids, HNO <sub>2</sub> and HNO <sub>3</sub> , respectively. <i>Indoor Activities</i> Stoves, heaters, fireplaces, and other sources of combustion. <sup>5</sup> Tobacco smoke. <sup>24, 25</sup> Dry-process photocopiers. <sup>26</sup> Degradation of cellulose nitrate objects. <sup>27, 28</sup>	• Affects the tarnishing of copper and silver by hydrogen
Indoor Activities Stoves, heaters, fireplaces, and other sources of combustion. <sup>5</sup> Tobacco smoke. <sup>24, 25</sup> Dry-process photocopiers. <sup>26</sup> Degradation of cellulose nitrate objects. <sup>27, 28</sup>	sulfide. <sup>37</sup>
Stoves, heaters, fireplaces, and other sources of combustion. <sup>5</sup> Tobacco smoke. <sup>24, 25</sup> Dry-process photocopiers. <sup>26</sup> Degradation of cellulose nitrate objects. <sup>27, 28</sup>	
Tobacco smoke. <sup>24, 25</sup> Dry-process photocopiers. <sup>26</sup> Degradation of cellulose nitrate objects. <sup>27, 28</sup>	
Dry-process photocopiers. <sup>26</sup> Degradation of cellulose nitrate objects. <sup>27, 28</sup>	
Degradation of cellulose nitrate objects. <sup>27, 28</sup>	
Construction Materials/Activities	
Generators and heavy equipment that use fuel- combustion engines.	

Boduced Culture Commenteds		- II C doctrons immotions alout tions / walnumt for not
		<ul> <li>n<sub>2</sub>&gt; desuroys infiniture plant ussue (relevant for hat- ural history or botanical collections).<sup>44</sup></li> </ul>
hydrogen sulfide (H <sub>2</sub> S)	Natural Sources	Lead Pigments: carbonates. hvdrocerussite or lead
carbonyl sulfide (COS) carbon disulfide (CS <sub>2</sub> )	Volcanoes, geothermal steam, geysers, sulfur wells, hot springs. <sup>38</sup>	white, and <b>oxides</b> , e.g., red lead pigment, are susceptible to darkening by $H_2^{S}$ .
Hydrogen sulfide smells like rotten eggs. It is responsible for that smell common to hot springs, as well as the	Oceans, seas, marine areas. <sup>39, 40</sup> Marshes, soils, wetlands. <sup>8</sup>	Metals:     Copper metal exposed to H <sub>2</sub> S develops a black copper     culture construction content of
sewer smen mouced at waste water treatment prants. Hydrogen sulfide is extremely toxic to people; fortu- nately, its odor can be detected at very low concentra- tions. 1 ppb. Collections are susceptible to reduced sulfur	Biological activity, decomposition of organic material, release from vegetation. <sup>39</sup> Biomass burning, forest fires, tropical forests.	basic copper suffate <sup>36</sup> Extremely damaging to <b>silver</b> and its salts; tarnishes sil- ver objects; reacts with silver salts in photographs;
compounds at even lower levels, ppt.	Industrial Processes	reacts with silver inlays, silver gift, etc. <sup>43,44</sup> , <sup>44</sup> Reacts with <b>bronz</b> , <b>lead</b> , <sup>49</sup> has a synergistic effect with
	Fuel and coal combustion. <sup>8</sup>	$NO_2$ to corrode <b>zinc</b> (see $NO_2$ ).
	Production of viscose rayon, vulcanization of rubber, etc. <sup>41</sup>	<ul> <li>Black-and-white photographs: reduced sulfur com- pounds and oxidants cause silver mirroring as well as redox sonts <sup>151</sup></li> </ul>
	Petroleum production, paper processing, wood pulping. <sup>8</sup>	• Low-fire ceramics. <sup>50</sup>
	Atmospheric Chemistry	• Stone, especially interior building stone. <sup>51</sup>
	$\rm H_2S$ and COS can be formed by the oxidation of carbonyl disulfide. $^{39}$	• Leather (see sulfur dioxide).
	INDOOR SOURCES	
	Collections and Objects	
	Mineral specimens that contain pyrite (iron sulfide, FeS <sub>2</sub> ); sulfate-reducing bacteria in waterlogged objects. <sup>8</sup>	
	Display Case Materials	
	Off-gassing from sulfur-containing proteins in materials used in exhibition and display case design, especially silks, wools, and felts. <sup>43</sup>	
	Adhesives, especially those made from animal hide, such as rabbit skin glue.	
	Construction Materials/Activities	
	Arc welding can be a significant source during a renovation. <sup>8</sup>	
	Flooring Materials Wool carnets 44	

Gaseous Pollutants	Major Sources (and Some Minor Sources)	At-Risk Museum Materials
	Strong Oxidizing Pollutants	
Ozone (O <sub>3</sub> ) A mior conditional of smorthast directly affects records	Ozone-specific Sources	Artists' colorants: fading of <b>dyes</b> and <b>pigments.</b> <sup>16, 31, 64, 65, 66</sup>
A major constituent of sinog that directly affects people, plants, and property. <sup>69</sup>	OUTDOOR SOURCES Smog: tropospheric (ground-level) ozone is a major sec-	Oxidation of organic compounds with double bonds, e.g., embrittles and cracks <b>rubber.</b> <sup>67, 68</sup>
Peroxyacetyl Nitrate (PAN) (CH <sub>3</sub> -COO-O-NO <sub>2</sub> )	טווטמוץ אטווענמוור טו עפוווכטומר מוט וווטטטוומו פווווזאטטוא.	<b>Electrical wire coatings</b> (of concern to industrial collections) <sup>69</sup>
A principal secondary pollutant in photochemical smog.	INDOOR SOURCES Office/building equipment, including dry-process photo-	<b>Plants</b> (of concern to botanical and natural history collections). <sup>70</sup>
Peroxides (–O:O –)	copiers. <sup>26, 52</sup> r1	Embrittles fabrics, textiles, and cellulosic materials. <sup>71</sup>
The simplest is hydrogen peroxide, HO:OH. It is the oxygen-oxygen bond that is extremely reactive.	electrical arcing, including electrostatic air cleaners, "	Enhances tarnishing of <b>silver</b> by reduced sulfur compounds.
Strong oxidizing pollutants present a great risk to collec- tions. Oxidants break down the structure of organic	PAN-specific Sources	Causes discoloration of <b>photographic prints.</b> <sup>151</sup>
materials by attacking carbon-carbon double bodans materials by attacking carbon-carbon double boda. This weakens the material and eventually if deferiorates	OUTDOOR SOURCES	Attacks paint binders. <sup>72</sup> Affects leather nerchment and animal skins (of concern
Oxidants can also react with other gaseous pollutants,	Secondary pollutants from urban traffic emissions <sup>54, 55</sup>	to natural history collections).
such as NOX, to create acidic analogs; radicals such as the hydroxy radical, OH*, and other reaction byproducts that are destructive, e.g., oxidation of aldehydes into acetic acid (see organic carbonyl pollutants entry).	produced by gas-phase reactions between hydrocarbons and nitrogen oxide compounds <sup>56, 57</sup> and reactions between organic carbonyl pollutants and the hydroxy radical (OH <sup>•</sup> ). <sup>58, 59, 60, 61</sup>	Adsorbed onto <b>building products</b> (plasterboards, painted walls, carpet, linoleum, pinewood, and melamine-covered particleboard), where it can react with and damage sur-
- - -	Pollutants from ethanol-fueled vehicles increase PAN production. <sup>62</sup>	taces or be rereleased into the environment. Rapidly fades certain <b>ink-jet print dyes.</b> <sup>151</sup>
	Forest fires. <sup>63</sup>	
	Peroxide-specific Sources	
	OUTDOOR SOURCES	
	Secondary pollutant generated by nitrogen oxide chemi- cal reactions with hydrocarbons, VOCs, and organic car- bonyl pollutants.	
	Byproduct of atmospheric reactions of pollutants from gasohol fuels. <sup>62</sup>	
	INDOOR SOURCES <sup>8</sup>	
	Emission from deterioration of organic materials, e.g., rubber floor tiles.	
	Oil-based paints.	
	Microorganism activities.	

	Organic Carbonyl Pollutants: Aldehydes and Organic Acids		
Organic Carbonyl Pollutants Aldehydes Formaldehyde (HCHO)	General sources for organic carbonyl pollutants (see also sources specific to formic acid and acetic acid, aldehydes, and formaldehyde)	<b>Metal</b> corrosion: non-noble metals such as <b>leaded</b> - bronzes, <b>copper alloys</b> . <sup>68</sup> Base metals such as <b>lead</b> , <b>cop</b> - <b>per</b> , <b>silver</b> . <sup>101</sup> Corrosion of <b>cabinetry hardware</b> coated with cadmium, lead, magnesium, and zinc. <sup>108</sup>	
Acetaldehyde (CH <sub>3</sub> CHO) Oreanic Acids	OUTDOOR SOURCES	Acid hydrolysis of <b>cellulose</b> reduces the degree of poly- merization, which is discernible as embrittlement.	
Formic Acid (HCOOH) Acetic Acid (CH <sub>3</sub> COOH)	<i>Atmospheric Chemistry</i> Secondary pollutants resulting from atmospheric reac- tions with industrial and vehicle pollutants. <sup>73, 74, 75, 76, 77</sup>	Attacks <b>calcareous materials</b> : land shells and seashells (i.e., Byne's Disease), corals, limestone, calcium-rich fossils. <sup>68</sup>	
Most materials damage by organic carbonyl pollutants is	Precipitation: gases concentrate in fog, rain, and snow. <sup>78</sup>	Low-fire ceramics. <sup>68, 109</sup>	
attributed to acetic acid or to formaldehyde. It is sus- pected that damage credited to formaldehyde is actually due to its oxidized form, formic acid.	Natural Sources Biogenic emissions from vegetation <sup>79</sup>	<ul> <li>Reacts with enamel and glass, especially previously damaged and weakened glass, such as weeping glass.<sup>110</sup></li> </ul>	
correspondingly, oxination of accardencing extrements acetic acid. However, the risk from direct emissions of acetic acid is greater.	<ul> <li>Biomass burning, forest fires, rainforest slash and burn, etc.<sup>80, 114</sup></li> </ul>	Stained glass: corrodes <b>lead joins</b> between glass panes.	
(See also specific entries for organic acids, aldehydes, and formaldehyde.)	Biodeterioration of organic materials.		
	INDOOR SOURCES		
	Gas-Phase Reactions		
	Indoor reactions of outdoor pollutants that infiltrate buildings. <sup>81</sup>		
	<ul> <li>Evaporation from hot water, e.g., dishwashers, showers.<sup>82, 83</sup></li> </ul>		
	Construction and building materials, especially materials used in the construction of display cases and storage cabinets. <sup>68, 84</sup> Laminated materials. <sup>85</sup>		
	<ul> <li>Coatings, sealants, paints and adhesives, some polyvinyl acetate adhesives, oil-based paints.<sup>86</sup></li> </ul>		
	<ul> <li>New houses (in older houses off-gassing has decreased significantly or ceased): Materials used in cabinet mak- ing.<sup>87</sup> doors, and plywood subfloors as well as assem- blies of floors.<sup>88, 89</sup></li> </ul>		
	<ul> <li>Materials manufactured with urea-formaldehyde, including foam insulation. Other formaldehyde-based resins such as phenol-formaldehyde wood products.<sup>5</sup>, 85, 90, 91, 92</li> </ul>		
	<ul> <li>Wood<sup>93, 94, 95</sup> and wood products.<sup>68, 86, 96, 97</sup></li> </ul>		

Gaseous Pollutants	Major Sources (and Some Minor Sources)	At-Risk Museum Materials
	Organic Carbonyl Pollutants: Aldehydes and Organic Acids	
	<ul> <li>Wood-based panel products, especially with urea-formaldehyde and melamine-formaldehyde binding resins;<sup>90</sup> e.g., pressed wood, composite wood panels, chip board, particle board, medium density fiberboard including Medite FR2<sup>®</sup>, parquet.<sup>98, 99</sup></li> <li>Other wood-based building materials.<sup>100, 101, 102</sup> <i>Flooring Materials</i></li> <li>Other wood-based building materials.<sup>100, 101, 102</sup> <i>Flooring Materials</i></li> <li>Flooring Materials</li> <li>Flooring innoleum, carpets.<sup>104</sup></li> <li>Other Materials</li> <li>Flooring, linoleum, carpets.<sup>104</sup></li> <li>Other Materials</li> <li>Flooring, linoleum, carpets.<sup>104</sup></li> <li>Plooring, linoleum, carpets.<sup>104</sup></li> <li>Flooring innoleum, carpets.<sup>104</sup></li> <li>Flooring innoleum, carpets.<sup>105</sup></li> <li>Flooring agents.<sup>105</sup></li> <li>Farniture and furniture coatings, varnishes.<sup>105</sup></li> <li>Paper and paper products.<sup>106</sup></li> <li>Finished fabrics.<sup>107</sup></li> </ul>	
Organic acids: acetic acid (CH <sub>3</sub> COOH)	General sources of both organic acids	(See at-risk materials in organic carbonyl pollutants entry.)
formic acid (HCOOH)	OUTDOOR SOURCES	
(See also organic carbonyl pollutants entry.)	Textile industry effluents and emissions. <sup>111</sup>	
	INDOOR SOURCES	
	Formaldehyde-free wood composite boards, e.g., Medex <sup>®</sup> and Medite $II^{\circledast}$ . Wooden structures. $^{152,153}$	
	Sources Specific to Formic Acid	
	Oxidation product from the reaction of formaldehyde with light. <sup>112</sup>	
	Sources Specific to Acetic Acid	
	Degradation of cellulose acetate objects. <sup>113</sup>	
	Silicone sealants. <sup>8</sup>	

Aldehydes:	OUTDOOR SOURCES	(See at-risk materials in organic carbonyl pollutants
formaldehyde (HCHO)		entry.)
acetaldehvde (CH_CHO)	industrial Frocesses	
(See also entries for organic carbonyl pollutants and formaldehyde.)	Primary pollutant from vehicles using alcohol fuels (e.g., methanol and gasohol) <sup>73, 115, 116</sup> and ethanol-gasoline fuel blends. <sup>117, 118</sup>	
	Automobile manufacturing, especially painting. <sup>119</sup>	
	INDOOR SOURCES	
	Combustion byproducts, cooking, heating, and tobacco smoke. <sup>6, 120</sup>	
	Artists' linseed oil paints and other drying oils. $^{121}$	
	Construction and Building Materials	
	Terra-cotta bricks. <sup>122</sup>	
	Ceramic manufacturing, kiln exposures. <sup>123</sup>	
	Vinyl, laminates, and wallpapers. Acrylic-melamine coatings. <sup>124</sup>	
	Alkyd paints. <sup>125, 126</sup>	
	Latex and low-VOC latex paints. <sup>127, 128, 129</sup>	
	Secondary pollutants produced by the reaction of ozone and some carpet materials. <sup>130</sup>	
Formaldehyde	Sources Specific to Formaldehyde	(See also at-risk materials in organic carbonyl pollutants
Formaldehyde is easily oxidized to formic acid, which is most likely the agressive chemical. <sup>112</sup>	INDOOR SOURCES	enuy.) Silver tarnish or surface discoloration. <sup>136</sup>
	Natural history wet specimen collections. Consumer products including: decorative laminates fiber-	<ul> <li>Reacts with unexposed photographic films as well as photographs</li> </ul>
	Sass products. <sup>85,131</sup>	to reduce silver ions in black-and-white photographs to
	Dry-process photocopiers. <sup>26</sup>	colloidal silver, causirig discoloration
	Textiles such as new clothes and fabrics, dry-cleaned clothes, permanent press fabrics, drapery, clothing, carpets, wall hangings, furniture coverings-unfinished fabrics. dveing process residues. chemical finishes. etc. <sup>107, 132</sup> .	<ul> <li>Cross-links proteins (e.g., collagen), resulting in loss of strength in animal hides, leather objects, parchments, etc. Also attacks objects with gelatin, animal glue, or casein binders.<sup>66</sup></li> </ul>
	133, 134	<ul> <li>Reacts with textiles, fibers.</li> </ul>
	<ul> <li>Fungicide in emulsion paints and glues, e.g., wheat pastes</li> <li>PVC-backed carpeting.</li> </ul>	<ul> <li>Attacks buffered papers and reacts with metallic-salt inclusion in paper.</li> </ul>
	Floor finishes, e.g., glitsa. <sup>135</sup>	<ul> <li>Discoloration of dyes, fading of organic colorants.<sup>137</sup></li> </ul>
	) - - -	• Chemically changes <b>inorganic pigments</b> , e.g., insoluble basic copper carbonate (main component of azurite) is converted to soluble copper acetate. <sup>138</sup>

Gaseous Pollutants	Major Sources (and Some Minor Sources)	At-Risk Museum Materials
	Other Potentially Damaging Pollutants	
Ammonia (NH <sub>3</sub> ) Ammonium ion (+NH <sub>4</sub> ) Most damage to museum collections is from the ammo- nium ion, produced when water and ammonia react.	OUTDOOR SOURCES <i>Natural Sources</i> Agriculture, especially fertilization, and animal wastes. <sup>139</sup> Animals are the largest global source of ammonia. <sup>140</sup> Biodeterioration, e.g., landfill gases. <sup>141</sup> Underground bac- terial activity. <sup>8</sup> <i>Industrial Processes</i> Fertilizer production. <sup>8</sup> INDOOR SOURCES <sup>8</sup> Household cleaning products. Museum visitors. Emulsion adhesives and paints. Alkaline silicone sealants. Concrete.	Blemishes <b>ebonite</b> . Blemishes <b>resins</b> . Reacts with materials made from <b>cellulose nitrate</b> , form- ing ammonium salts that corrode <b>metals</b> .
<b>Amines (R-NH<sub>2</sub>)</b> These alkali pollutants are derivatives of ammonia.	INDOOR SOURCES Amine-based corrosion inhibitors used in humidification systems and ventilation ducts. <sup>142, 143</sup> Atmospheric reactions of nitrogen species and alkali pollu- tants released from new concrete. <sup>144</sup> Epoxy adhesives. <sup>8</sup>	Causes blemishes on <b>paintings</b> , usually when the pollu- tant is dispersed through the ventilation system. <sup>143</sup> Corrosion of <b>bronze</b> , <b>copper</b> , and <b>silver</b> . Darkens <b>linseed</b> oil and forms copper amine complexes with <b>copper pigments</b> , e.g., malachite. <sup>144</sup>
Fatty Acids	OUTDOOR SOURCES Vehicle exhaust. <sup>8</sup> INDOOR SOURCES <sup>8</sup> Animal skins, furs, taxidermy specimens, and insect col- lections (relevant for natural history collections and parchment). Museum visitors. Combustion: burning candles, cooking. Adhesives. Linoleum.	Yellows <b>paper</b> and <b>photographic documents.</b> Corrodes <b>bronze, cadmium</b> , and <b>lead.</b> Blemishes <b>paintings.</b>

Hydrochloric Acid (HCl)	OUTDO Coal con Oceans,	OR SOURCES nbustion.1 sea-mist spray.	HCI is an acidic gas an especially under high- coastal regions. <sup>145</sup> Affects the tarnishing sulfide. <sup>37</sup>	nd attacks <b>acid-sensitive materials</b> , humidity conditions often present in of <b>copper</b> and <b>silver</b> by hydrogen
Water vapor (H2,O) Water vapor, i.e., relative humidity (R parameter for museum collections. Be effects of humidity changes on collect increases corrosion rates and decay ra in most chemical reactions.	OUTDO Atmosph sides the direct Bodies o tions, water vapor Bodies o ties and is involved INDOOF Fountain Humidifi People. Wet clea	OR SOURCES here (high-humidity days). f water. s SOURCES ers. .ning activities.	Increases hydrolysis re usually leads to damag weakens paper object; Increases hydrogen su <b>silver</b> . <sup>146</sup> Controlling factor in <b>B</b> Increases deterioratior corrosion, <sup>148</sup> effloresc photo-oxidation of <b>arl</b> Increases the fading <sup>14</sup> watercolors. <sup>150</sup>	actions on <b>organic objects</b> , which ge (e.g., hydrolysis of cellulose s). f nitrogen oxides on <b>photographs</b> . <sup>151</sup> Ilfide corrosion of <b>copper and</b> sronze Disease. <sup>147</sup> n of materials, e.g., <b>metal</b> ence of <b>calcareous</b> objects, and <b>tists' colorants</b> . <sup>9</sup> of <b>dyestuffs</b> used in textiles and
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Current Target Levels for Key Gaseous Pollutants in Museums<sup>a</sup>

Major <i>outdoor</i> pollutants found inside museums	Suggested Limits for ( ppl	Pollutant Collections b) <sup>b, c</sup>	Action Limi	ts <sup>d</sup> (ppb)	Air Qu Recommenda	lality tions (ppb)	Reference Concen	trations (ppb)			
	Sensitive materials <sup>e</sup>	Other materials in collections	High	Extremely high	Archival document storage <sup>15</sup>	Libraries, archives and museums <sup>16</sup>	Natural back- ground levels	Urban areas	Health: Acute toxicity level for 1-hr exposure	U.S. EPA Clean Air Act limits <sup>g</sup>	World Health Organization <sup>h</sup> TWA limits
Nitrogen dioxide, NO <sub>2</sub>	< 0.05- 2.6	2-10	26-1041	> 2601	Canada: 2.6 USA: 2.6	2.6	0.2–4.9 <sup>1</sup> 0.05–0.3 <sup>2, 3</sup>	1.6–68 <sup>4</sup> 10–47 <sup>1</sup> USA: 22–52 <sup>4</sup> Canada: 16–22 <sup>4</sup> Europe: 2–34 <sup>4</sup>	ОЕННА <sup>†:</sup> 246 OSHA <sup>i</sup> : 5 ppm	50 [1 yr]	104 [1 hr] 21 [annual] 62 [8 hr]
Nitrogen monoxide, NO (see ozone)							0.16 –1.6 <sup>4</sup> 1–21 <sup>5</sup>	1.6–32 <sup>5</sup>	OSHA: 25 ppm		
Acidic nitrogen gases, HNO <sub>2</sub> , HNO <sub>3</sub>	< 0.1	< 1.0					0.02-0.2 <sup>2</sup>	1–11 <sup>4</sup> 3–49 <sup>2</sup>	OEHHA (HNO <sub>3</sub> ): 33		
Ozone, O <sub>3</sub>	< 0.05	0.5-5	25-60	75-250	Canada: 1.0 USA: 13	2.0	1-100 <sup>4</sup>	5-200 <sup>1</sup> 20-150 <sup>1</sup> USA: 100-120 <sup>4</sup> Canada: 17-21 <sup>4</sup> Europe: 65-145 <sup>4</sup>	OEHHA: 90 OSHA: 100	120 [1 hr] 80	60 [8 hr]
Sulfur dioxide, SO <sub>2</sub>	< 0.04- 0.4	0.4-2	8–15	15-57	Canada: 0.4 USA: 0.4	1.0	0.04–11 <sup>4</sup> Rural: USA: 6–10 <sup>4</sup> Europe: 1–14 <sup>4</sup>	8–380 <sup>1</sup> 2–152 <sup>4</sup> USA: 4–6 <sup>4</sup> Canada: 4–6 <sup>4</sup> Europe: 2–94 <sup>4</sup>	OEHHA: 248 WHO: 19 OSHA: 5 ppm	30 [1 yr] 140 [24 hr]	190 [10 min] 10 [24 hr] 19 [annual]

Major i	<i>ndoor</i> -generated	Suggested Limits	Pollutant (ppb)	Action Lin	nits (ppb)	Reference Con	centrations (ppb)			
polluta museur	nts found in ms	Sensitive materials	Collections in general	High	Extremely high	Natural background levels	Urban areas	Health: Acute toxicity level for 1-hr exposure	U.S. EPA Clean Air Act limits	World Health Organization TWA limits
Ĥ	ydrogen sulfide, H <sub>2</sub> S	< 0.010	< 0.100	0.4–1.4	2.0–20	0.005–10 <sup>3</sup>	0.1 <i>–5<sup>6</sup></i> 0.080–0.150	OEHHA: 30 OSHA: 10 ppm		107 ppb
					Organic Carbony	I Pollutants				
ĕ spi ⊃iut	cetic acid CH <sub>3</sub> COOH	< 5	224 <sup>7, 8</sup> 40–280	200–480 <sup>9</sup>	600–1000 <sup>9</sup>	0.1-4 <sup>4</sup>	0.1–16 <sup>4</sup> , <sup>10</sup>	OSHA: 10 ppm		
이명 256 이 단	ormic acid <sup>k</sup> HCOOH	<ul><li>∧</li><li>√</li></ul>	5–20	20-120	150-450	0.05-4 <sup>11</sup> 0.05-0.2 <sup>4</sup>	0.05–17 <sup>10</sup> 0.6–104	OSHA: 5 ppm		
요 səpʎyə	ormaldehyde HCHO	< 0.1–5	10–20	16–120 <sup>9</sup>	160–480 <sup>9</sup>	0.4–1.6 <sup>2</sup>	1.6–24 <sup>12</sup> new home: 50–60 <sup>13</sup>	ОЕННА: 75 ОЅНА: 750		80 [30 min]
¥ PPI∀	cetaldehyde <sup>l</sup> , CH <sub>3</sub> CHO	< 1–20					3-17 <sup>12</sup>	OEHHA <sup>m</sup> : 5 OSHA: 200 ppm		
To	otal VOCs (as hexane) <sup>n</sup>		< 100 ppb	700 ppb	1700 ppb		New or renovated building 4500–9000 <sup>14</sup>			
<ol> <li>Work</li> <li>Work</li> <li>Seinf</li> <li>Grack</li> <li>Tétree</li> <li>Grack</li> <li>Grack</li> <li>Sano</li> <li>Sano</li> <li>Sano</li> <li>Sano</li> <li>Rank</li> <li>Crosi</li> <li>Rank</li> <li>Lavec</li> <li>NAFA</li> </ol>	d Health Organization 2000. eld 1984. eld 1984. ault 2003b. ean 1988. ean 1988. ean 1988. ean 1999. 1999. and Thickett 1999. ey and Thickett 1999. by and Christensen 1997. ean and Williams 1992. sen et al. 2000. wmura, Steinberg, and Schlatter 1992 arine 2002. v 2004.		<sup>a</sup> These are currer Concentrations (IAQ.db) website (IAQ.db) bMaximum levels and RH below 66 <sup>c</sup> Temperature and Mitigation meas <sup>e</sup> Sensitive materi, fAcute Reference <sup>b</sup> Vorld Health O <sup>1</sup> U.S. Department NO is unstable a nate O <sup>3</sup> very little is kno <sup>1</sup> U.title damage ha nate O <sup>3</sup> <sup>c</sup> Thronic REL ee <sup>m</sup> Chronic REL ee	in standards based on mits for materials an s allowed to ensure r 3% and ideally belov of relative humidity a sures should be taken as are those that are las are those that are to it Labor: Occupation rganization's maxim rganization's maxim rganization's maxim rganization's that support the effect to both the effect to californ teolished by Californ reported referenced	a the best available sour d objects continue to be ininimum risk to sensitive v 50% (Tétreault 2001). s well as pollutant conce in protect objects in th at risk from the particu LS) established by the C cy Office of Air and Rad um exposure recommen and Safety and Health A However, it reacts with However, it reacts with However, it reacts with e of formic acid at variou uted to acetaldehyde. ia OEHHA (2005).	ces and are not meant t reviewed. Two source s objects; assumes a tern entration should always e collection. Iar gaseous pollutant; se alifornia Office of Envir lar gaseous pollutant; se alifornia Office of Envir iation Clean Air Act limi iation Clean Air Act limi iation Clean Air Act limi ation Clean Air Act limi ozone to form HNO <sub>2</sub> , n ozone to form HNO <sub>2</sub> , n s concentrations.	o be absolute and final co s are CCI (www.cci-icc.gc.c perature between 15°C ar be minimized to reduce ris e Appendix 1. onmental Health Hazard A t (U.S. EPA 1990). Srganization 2000). sible Exposure Limit (PEL) itrous acid, which is dama	rcentration recommendations ca) or the IAQ in Museums an 1d 25°C, cleanliness of the col k. ssessment (California OEHHA ssessment (California OEHHA ging. To reduce the risk from I	Id Archives lection, 2000). NO, elimi-	

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Appendix 3 Materials Testing

#### Materials Testing

The tests described below, although time consuming, are effective at identifying potentially damaging display and construction materials before they are used where they might come in contact with collections. However, the tests have certain drawbacks. If a material passes one test, this does not mean it is safe with respect to all gases and for all objects. Materials must be tested for all compounds that could pose a risk. For example, if a board marketed as zero-formaldehyde passes the Chromatropic Acid Test for formaldehyde, it cannot be assumed that it will also pass the Iodide-Iodate Test for volatile acids, especially organic acids.

In addition, manufacturers change processing and formulations of their products without warning, often resulting in batch-to-batch variability in materials characteristics. It is not unusual to find that a sample of a material being considered for a display case passes the various tests, but when the lot arrives, the material fails on retesting. Testing of a sample from the bulk order prior to use is highly recommended.

			Positive Test	
Test	Description	Identifies	Indication	Reference
Beilstein Test	Flame test with small bit of material on hot copper wire	Presence of chloride in plastics	Green flame	CCI 1993
Calcium hydroxide (lime) water and pH paper	Determine the pH of 1 g of sample material mixed with the lime water	Presence of volatile acids, including organic acids	pH of solution in tube with sample will be lower than that of a control	Odegaard, Carroll, and Zimmt 2000
Chromatropic Acid Test	Reaction with 2 g of material	Presence of formaldehyde and aldehydes	Yellowish solution turns blue	Green and Thickett 1996; Zhang, Thickett, and Green 1994
Glycerol and pH paper	Determine the pH of 1 g of sample material	Presence of volatile acids including organic acids	pH of solution in tube with sample will be lower than that of a control	Odegaard, Carroll, and Zimmt 2000
Iodide-Azide Test (sodium azide test)	Spot test on sample material	Presence of reduced sulfur compounds, e.g., H <sub>2</sub> S	Generation of nitrogen gas bubbles	Daniels and Ward 1982
Iodide-Iodate Test	Reaction with 2 g of material	Presence of volatile acids, including organic acids	Colorless solution turns blue	Green and Thickett 1996; Zhang, Thickett, and Green 1994
Oddy metal coupon test (copper)	Copper coupon exposed with sample of material	Chlorides, HCl, oxides such as $SO_2$ , $NO_2$ , NO, and sulfur compounds	Surface corrosion or discoloration (compare with control)	Oddy 1973; Green and Thickett 1996; Zhang, Thickett, and Green 1994

Oddy metal coupon test (lead)	Lead coupon ex- posed with sample	Aldehydes, organic acids, acidic gases	Surface corrosion or discoloration (com- pare with control)	Same as above
Oddy metal coupon test (silver)	Silver coupon ex- posed with sample of material	Presence of reduced sulfur compounds, e.g., H <sub>2</sub> S or carbonyl sulfide	Surface corrosion or discoloration (compare with control)	Same as above
Electronic meter or pH paper	pH measurement of cold aqueous extraction of 1 g of material	Presence of strong or weak acidic gases	pH less than 4	Tétreault 1992a TAPPIª Method T 509 om-02
Electronic pH meter	Nondestructive, electronic reading	Presence of acids or bases	Meter reading indicates pH	TAPPI Method T 529 om-99
pH pens	Line marked on sample using Abbey pH pen <sup>b</sup> or pH pen <sup>c</sup>	Presence of acids or bases	Observe color development	Odegaard, Carroll, and Zimmt 2000
Phloroglucinol-HCl test	Spot test on sample of material	Presence of lignin, which makes paper unstable to light and may contribute to acidity.	Red/purple color indicates that lignin is present	Rhyl-Svendsen 2001

Source: Compiled after Ryhl-Svendsen 2001 and Odegaard, Carroll, and Zimmt 2000. See also IAQ in Museums and Archives, http://iaq.dk/papers/tests.htm; Tétreault 2003a; and Hatchfield 2002 for more material testing descriptions. Notes:

<sup>a</sup> Technical Association of the Pulp and Paper Industry, Inc. (www.tappi.org).

<sup>b</sup> Abbey pH pen is available at University Products, Holyoke, Mass., or Preservation Equipment, U.K.

<sup>c</sup> pH Pen is available from Light Impressions, Rochester, N.Y., or Preservation Equipment, U.K.

# Appendix 3

# Protocols for Preparing and Analyzing Passive Sampling Devices for Organic Carbonyl Pollutants

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### Introduction

These protocols describe both the preparation and the analysis of selected samplers for organic carbonyl pollutants, specifically, formaldehyde and organic acids. The analytical protocols, developed in the GCI Air Pollution Analysis Laboratory, can be modified according to the design requirements of the monitoring program and specific laboratory instrumentation. The protocols can be used in-house, or they can be included with samplers sent to an independent laboratory. Even if samples are sent to a laboratory for analysis, it is useful to become familiar with the preparation and analysis procedures in order to judge the results more effectively. Before embarking on the protocols, please review the following general cautions.

- 1. Laboratory Conditions. Preparation and analysis of passive sampling devices for organic carbonyl pollutants must be conducted in a laboratory free of organic acids, aldehydes, or ketones (e.g., acetone) to minimize background contamination of the analytes of interest. This is especially critical for the detection of ppb concentrations of organic carbonyl pollutants.
- 2. Health and Safety. Review Material Safety Data Sheets for all chemicals, and use appropriate personal protective equipment. Work in a fume hood, and follow good laboratory and safety practices at all times.
- 3. Chemical Quality. All chemicals should be HPLC grade or American Chemical Society (ACS) reagent grade or better. Use HPLC grade water or Milli-Q water<sup>1</sup> for DNPH samplers and analysis. Ultra pure water quality is critical for preparation and analysis of organic acid samplers. Use only Milli-Q water or equivalent.

### Part 1. Preparation of Organic Acids MDTs

The organic acids MDTs, which detect pollutant concentrations at the ppb level, were the first passive samplers designed specifically for the museum field. Gibson et al. (1997a, 1997b) developed the organic acids MDTs. The organic acids MDT is based on the Palmes open-path diffusion tube housing. The organic acids MDT is assembled with potassium hydroxide solution applied to stainless steel meshes. Organic acids in the air diffuse through the static air layer in the tube and are trapped by acid-base interactions. The clear acrylic tubes are capped with blue caps to distinguish them from the formaldehyde MDTs that use red caps. The pollutants are trapped as ions, washed from the meshes, and analyzed by ion chromatography (IC) to determine the concentration of organic acids in air.

The original protocol for preparing these samplers was modified slightly by the GCI laboratory in conjunction with a collaborative inter- and intralaboratory study in 1997–98 with Lorraine Gibson at the University of Strathclyde and Agnes Brokerhof at the Netherlands Institute for Cultural Heritage (ICN) (Grzywacz and Villata 1998, 1999).

# Supplies and Chemicals for Preparing Organic Acids MDTs

- Palmes open-path diffusion tube housing: clear polymethylmethyacrylate tubes (7.1 cm × 1.1 cm) open at both ends, one end blunt and the other tapered; clear acrylic caps; blue acrylic caps and stainless steel mesh disks (Gradko International Ltd., U.K.).
- potassium hydroxide pellets
- ethylene glycol dimethyl ether, 99.9%, HPLC grade
- Milli-Q water or equivalent
- Ion Chromatography Acrodisc<sup>®</sup> 13 mm syringe filters, 0.2 µm pore-size Supor<sup>®</sup> membrane

### **Preparation of KOH Trapping Solution**

- 1. Prepare approximately 1 molar solution of potassium hydroxide in Milli-Q water. Weigh 5.6 g of KOH pellets in a 100 mL beaker, then dissolve by adding 70 mL of Milli-Q water. Caution: the solution may become warm.
- 2. Measure 10 mL of ethylene glycol dimethyl ether in a graduated cylinder. This is a very smelly chemical; work with it in the fume hood.
- 3. Decant the ether into the KOH solution and mix with a glass stirring rod.
- 4. Transfer this solution into a 100 mL volumetric flask, let it cool to room temperature, then fill to the mark with Milli-Q water.

#### **Quality Control of KOH Trapping Solution**

Analyze the trapping solution before using it to make the organic acids MDTs. Take 40  $\mu$ L of the trapping solution and dilute it in 5.0 mL Milli-Q water. Filter as described in Part 6; analyze as described in Part 2.

# Assembly of Organic Acids MDTs

The KOH MDTs should be prepared as close as possible to the actual deployment day. Use clean tubes, stainless steel meshes, and caps (see cleaning instructions in Part 6).

Determine the number of MDTs required. Each monitoring location requires the preparation of three tubes: two for exposure and one blank. In addition to MDTs that will be exposed, laboratory MDT blanks must be prepared. These never leave the laboratory. They will be analyzed to determine the batch background amounts of acetate and formate. The number of laboratory blanks is at least three or the square root of the total number of samplers prepared for monitoring.

- 1. In a fume hood, place the correct number of blue caps, clear caps, and tubes on a clean, absorbent surface (e.g., Versi-Dry) or paper towels.
- 2. Insert two clean stainless steel mesh disks into each blue cap.
- 3. Pipette 40.0  $\mu$ L of the trapping solution into each blue cap. Make sure that the solution is distributed evenly over the surface of the steel meshes. Use another pipette tip to spread the solution over the disks, if necessary.

- 4. Leave the coated caps in the fume hood to dry for about two hours.
- 5. Assemble the organic acids MDTs by (1) pushing the colorless cap onto the flat, blunt end of the acrylic tube and (2) pushing the tapered end of the tube into the blue cap with the KOH loaded stainless steel frits.
- 6. Store the organic acids MDTs in the refrigerator until ready to deploy. Refrigerate the laboratory blanks until you are ready to analyze them.

# Part 2. IC Analysis of Organic Acids MDTs

# Supplies and Chemicals

- sodium tetraborate decahydrate, ACS reagent grade 99.5–105.0%
- Milli-Q Water
- ultrasonic cleaner
- 10 mL beakers
- sodium formate (formic acid sodium salt)
- sodium acetate (acetic acid sodium salt)
- Ion Chromatography Acrodisc<sup>®</sup> 13 mm syringe filters 0.2 µm pore-size Supor<sup>®</sup> membrane. Note: It is very important to use the correct filters for ion chromatographic analysis.

### Instrumentation

A Dionex 500 Ion Chromatography system with Peak Net Software is used to analyze acetic acid and formic acid trapped on organic acids MDTs. Ion suppression is used to improve the detection of ionic analytes (acetate and formate) with a conductivity detector. Borax mobile phase at 1.0 mL·min<sup>-1</sup> through an Ionpac<sup>®</sup> ICE-AS6 ion-exclusion column,  $9 \times$ 250 mm, is used to separate the components. For both calibration standards and samples, 50 µL injection volumes are used.

#### Preparation of Borax Mobile Phase

To prepare the stock solution of 50.0 mM Borax:

- 1. Weigh 19.1g of the dry borax salt, sodium tetraborate decahydrate, and place in a beaker with about 800 mL of Milli-Q water, and gently heat until it is completely dissolved.
- 2. Transfer the solution into a 1 L volumetric flask, and let it cool overnight before filling it to the mark with Milli-Q water.

To prepare the IC mobile phase: 6.0 mM borax solution:

1. Dilute 240 mL of the stock 50.0 mM borax solution in a 2 L volumetric flask. Fill to the mark with Milli-Q water. Transfer this to the mobile phase bottle.

### Preparation of Standards and Calibration

Prepare 1.00 mg·mL<sup>-1</sup> stock solutions of acetate and formate:

- 1. Accurately weigh 1.389 g sodium acetate.
- 2. Transfer to a 1 L volumetric flask and dissolve with Milli-Q water.
- 3. Weigh 1.511 g sodium formate, and dissolve with Milli-Q water in a 1 L volumetric flask.

Sodium salts of formic acid and acetic acid are used to prepare the standards. The weight measured is the weight of the sodium salt. We want to know the weight of the formate and acetate ions in solution, not the sodium salts. Percent of acetate in sodium acetate is determined as follows (similarly for percent of formate in sodium formate):

$$wt_{acetate} = wt_{sodium acetate} \times MW_{acetate} \div MW_{sodium acetate}$$

where the molecular weight (MW) of acetate is 59.04 g·mol<sup>-1</sup>, and the MW of sodium acetate is 82.03 g·mol<sup>-1</sup>.

$$MW_{acetate} \div MW_{sodium acetate} = 59.04 \text{ g} \cdot \text{mol}^{-1} \div 82.03 \text{ g} \cdot \text{mol}^{-1} = 0.720$$

For sodium acetate: We weighed 1.389 g sodium acetate and 72.0% sodium acetate is acetate; hence, 1.389 g sodium acetate is equivalent to 1.000 g acetate, and we have prepared a stock solution of 1.000 g·L<sup>-1</sup> or 1.000 mg·mL<sup>-1</sup>.

Similarly for sodium formate: The MW of formate is 45.01 g·mol<sup>-1</sup>, and MW of sodium formate is 68.01 g·mol<sup>-1</sup>. Thus, 66.2% of sodium formate is formate. 1.511 g sodium formate in 1 L is equivalent to 1.0 g formate per liter or 1.0 mg·mL<sup>-1</sup>. Store the stock solutions in the refrigerator until ready to use.

Daily calibrants are prepared by diluting the stock solution using Milli-Q water. The concentration of the daily solutions should be 1, 2, 3, 4, and 5  $\mu$ g·mL<sup>-1</sup>. Using 100 mL flasks, the volume of stock solution required in the five flasks is 100, 200, 300, 400, and 500  $\mu$ L each of the sodium acetate and sodium formate stock solutions. Aliquots are then filtered into the autosampler vials with Ion Chromatography Acrodisc<sup>®</sup> 13 mm syringe filter with 0.2  $\mu$ m pore-size Supor<sup>®</sup> membrane; see filtering in Part 6.

Once the standards have been analyzed, check that the calibration graph is linear. Save these data with the analyses for the day.

### **Sample Preparation**

The trapped acetate and formate has to be washed from the active surfaces (stainless steel meshes) with Milli-Q water. After the samples are filtered, they are ready for analysis. Prepare only the number of samplers that can be analyzed the same day.

- 1. Remove the organic acids MDTs from the refrigerator and allow them to warm to room temperature.
- 2. Set out Versi-Dry in the fume hood.
- 3. Remove the blue caps from the clear tube. Tap the stainless steel mesh disks from the cap into a clean and dry 10 mL beaker.

- 4. Rinse the blue cap with five 1.000 mL aliquots of Milli-Q water into the 10 mL beaker with the stainless steel mesh disks.
- 5. Sonicate the beaker for 1 minute.
- 6. Filter the sample using Ion Chromatography Acrodisc<sup>®</sup> 13 mm syringe filters 0.2 µm pore-size Supor<sup>®</sup> membrane into an autosampler vial.

### Analysis of Samples

Analyze with instrumental setup described above. Calibrate the system using 50  $\mu$ L injection volumes. Analyze 50  $\mu$ L of each sample and blank. The software will determine the  $\mu$ g·mL<sup>-1</sup>.

### Calculating Acetic Acid and Formic Acid Concentrations

1. Adjust for dilutions or different injection volumes. For example, if a sample was diluted in half because it was too concentrated, multiply the computer reported  $C_{sample}$  in  $\mu g \cdot m L^{-1}$  by 2.

$$C_{sample} \times V_{standard injection volume} \div V_{injected} = C_{sample-standard injection volume}$$

 $C_{sample} \times Dilution Factor = C_{sample-dilution corrected}$ 

### 2. Calculate net concentration.

*MDT laboratory blanks:* Calculate the average and standard deviation of the concentrations of formic acid and acetic acid detected on the laboratory blanks. These should be zero. If analyte is detected, average the concentrations detected on the laboratory blanks. These will be subtracted from concentration reported for each tube analyzed from the same batch.

$$C_{tube-1} - C_{lab-blank} = C_{tube-1 adj}$$
$$C_{tube-2} - C_{lab-blank} = C_{tube-2 adj}$$
$$C_{blank-tube} - C_{lab-blank} = C_{blank-tube adj}$$

Organic acids MDTs: Subtract the concentration detected on the location blank ( $C_{blank-tube}$ ) from the concentration detected on each of the two tubes deployed at the same location,  $C_{tube-1}$  and  $C_{tube-2}$ , to obtain net concentrations in  $\mu g \cdot m L^{-1}$ . If required, use the adjusted tube concentrations from the previous step.

$$C_{tube-1} - C_{blank-tube} = C_{tube-1 net}$$
  
 $C_{tube-2} - C_{blank-tube} = C_{tube-2 net}$ 

3. Determine amount of trapped pollutant (acetate and formate). Multiply the net concentration ( $C_{tube-1 net}$ ,  $C_{tube-2 net}$ ) in  $\mu g \cdot m L^{-1}$  by the wash volume ( $V_{wash}$ ), which is 5.0 mL for organic acids MDTs, to obtain the amount in  $\mu g$  of acetate or formate per sampler.

$$C_{\text{tube-1 net}} \mu g \cdot m L^{-1} \times V_{\text{wash}} m L = C_{\text{tube-1}} \mu g \cdot \text{tube}^{-1}$$

 $C_{tube-2 net} \mu g \cdot m L^{-1} \times V_{wash} m L = C_{tube-2} \mu g \cdot tube^{-1}$ 

The analysis quantifies the amount of anion trapped on the MDT. We want to know the amount of organic acid in the air. For this reason, we must convert the measured µg amount of acetate or formate to µg acetic acid and formic acid trapped on each tube by multiplying the amount of acetate or formate by the ratio of their molecular weights:

$$C_{acetic acid tube-1} = C_{acetate tube-1} \times MW_{acetic acid} \div MW_{acetate}$$

$$C_{acetic formic tube-1} = C_{formate tube-1} \times MW_{formic acid} \div MW_{formate}$$

where MW acetic acid =  $60.04 \text{ g} \cdot \text{mol}^{-1}$ ; MW acetate =  $59.04 \text{ g} \cdot \text{mol}^{-1}$ ; Ratio = 1.017

and MW formic acid = 46.01 g·mol<sup>-1</sup>; MW formate = 45.01 g·mol<sup>-1</sup>; Ratio = 1.022.

#### 4. Determine volume of sampled air.

Calculate the volume of sampled air (V<sub>air</sub>) by multiplying the exposure time in minutes (T<sub>exp</sub>) by the device's sampling rate (SR) in mL·min<sup>-1</sup> for the specific pollutant (see table A4.1). Multiply by  $10^{-6}$  m<sup>3</sup>·mL<sup>-1</sup> to convert the volume from mL to cubic meters.

$$T_{exp} \times SR \times 10^{-6} \text{ m}^3 \cdot \text{mL}^{-1} = V_{air} \text{ in } \text{m}^3$$

#### Table A4.1.

PSD sampling rates. Because of the physics of diffusion, sampling rates vary by device and by pollutant. In general, the larger, heavier molecules have slower sampling rates.

Passive Sampling Device	Pollutant	Sampling Rate	Exposure Range
GMD Formaldehyde Dosimeter badge	formaldehyde	25.2 mL·min <sup>-1*</sup> RSD 6.7%	15 minutes– 24 hours
GMD Formaldehyde Dosimeter badge (Brown et al. 1994)	acetaldehyde	8.0 mL⋅min <sup>-1</sup>	15 minutes– 24 hours
University of Strathclyde Formaldehyde MDT (Gibson and Brokerhof 2001)	formaldehyde	1.34 mL∙min <sup>-1</sup> RSD < 7%	7–28 days
University of Strathclyde Organic acids MDT (Gibson et al. 1997a, 1997b)	acetic acid	1.02 mL∙min <sup>-1</sup>	7–28 days
University of Strathclyde Organic acids MDT (Gibson et al. 1997a, 1997b)	formic acid	0.88 mL∙min <sup>-1</sup>	7–28 days
Notes: *Scott-Bacharach, Inc., Manufacturer, Analysis (Pittsburgh, Pa.: Bacharach, I	570 Series Formaldahyde nc., 1993).	Dosimeter Badge: Instructio	ons for Use and Sample

5. Determine pollutant concentration in  $\mu g \cdot m^{-3}$  and convert it to ppb. Divide the  $\mu g$  amount of each analyte detected per tube 1 and tube 2 by the volume of sampled air ( $V_{air}$ ) to obtain the amount of pollutant per m<sup>3</sup> of air. Average the concentration determined on each tube to report the pollutant concentration in air at the location sampled:

$$C_{\text{acetic acid tube-1}} \div V_{\text{air}} = C_{\text{acetic acid-1 air}} \ \mu g \cdot m^{-3}$$
$$C_{\text{acetic acid tube-2}} \div V_{\text{air}} = C_{\text{acetic acid-2 air}} \ \mu g \cdot m^{-3}$$

$$(C_{\text{acetic acid-1 air}} + C_{\text{acetic acid-2 air}}) \div 2 = C_{\text{acetic acid air}} \text{ in } \mu g \cdot m^{-3}$$

Repeat for formic acid if detected.

Use the conversion factor in table 3.1 or the online concentration converter (http://www.iaq.dk/papers/conc\_calc.htm) to convert  $\mu g \cdot m^{-3}$  to ppb.

### Part 3. Preparation of Formaldehyde MDTs

Gibson and Brokerhof (2001) developed a PSD to trap formaldehyde present in the air based on the Palmes open-path diffusion tube housing. The University of Strathclyde formaldehyde MDT uses a filter paper disk impregnated with 2,4-dinitrophenylhydrazine (DNPH) as the trapping surface or active surface. The clear acrylic tubes are capped with red caps to indicate they are for formaldehyde. Blue-capped tubes are for organic acids; see Part 1.

DNPH is used to monitor for formaldehyde since it selectively reacts with aldehydes and ketones in a nucleophilic attack on the carbonyl carbon with a 1,2-elimination of water to form the aldehyde-2,4dinitrophenylhydrazone derivative. High performance liquid chromatography (HPLC) is used to quantify the amount of formaldehyde-2,4-dinitrophenylhydrazone (F-DNPH) trapped on the sampler. If desired, other carbonyl-2,4-dinitrophenylhydrazone derivatives, for example, acetaldehyde-2,4-dinitrophenylhydrazone can be quantified as long as sampling rates have been determined for the specific carbonyl pollutant with the particular PSD.

#### Supplies and Chemicals for Preparation of Formaldehyde MDTs

- Palmes open-path diffusion tube housing: clear polymethylmethyacrylate tubes (7.1 cm × 1.1 cm) open at both ends, one end blunt and the other tapered; clear acrylic caps; and red acrylic caps (Gradko International Ltd., U.K.)
- Filter paper discs: Whatman<sup>®</sup> Laboratory Products Antibiotic Assay Disks, Grade AA, 1.1 cm diameter
- HPLC-grade acetonitrile
- Orthophosphoric acid, concentrated, 85%

- Twice recrystallized 2,4-dinitrophenylhydrazine (if desired, this can be prepared in-house; see instructions in Part 6)
- Pall<sup>®</sup> Life Sciences LC Minispike Acrodisc<sup>®</sup> 13 mm syringe filters, 0.2 μm pore-size PTFE membrane

# Preparation of DNPH Trapping Solution

The following makes approximately 10 mL of trapping solution, enough for more than 150 tubes.

- 1. In a 25 mL Erlenmeyer flask, dissolve 300 mg twice recrystallized 2,4-DNPH in 10.5 mL acetonitrile.
- 2. Add 0.5 mL concentrated phosphoric acid. The crystals are fully dissolved by gently heating the solution to approximately 50°C.
- 3. Transfer the solution into a clean 20 mL glass vial and store in a laboratory explosion-proof refrigerator until ready to use.

### **Quality Check of DNPH Trapping Solution**

Before preparing the formaldehyde MDTs, an aliquot of the trapping solution is analyzed by HPLC to measure the concentration of DNPH as well as the background levels of formaldehyde-DNPH (F-DNPH) and other carbonyl-DNPH for the pollutants of interest.

- 1. Remove the DNPH trapping solution from the refrigerator and allow it to warm to room temperature.
- 2. Dilute 60.0 µL in 3.00 mL of HPLC grade acetonitrile.
- 3. Using an LC Minispike Acrodisc<sup>®</sup> 13 mm syringe filter, 0.2 µm poresize PTFE membrane, filter the solution into an autosampler vial as described in Part 4.
- 4. Analyze with the analytical method for DNPH described in Part 2.
- 5. Aldehyde-2,4,dinitrophenylhydrazones should not be present. The only peak should be the reagent peak: 2,4-dinitrophenylhydrazine. If there are significant peaks for the aldehyde-DNPHs, especially formaldehyde-2,4,-dinitrophenylhydrazones, it is advisable to discard the trapping solution and prepare fresh solution.
- Document the DNPH peak area (PA) per microliter (μL) of trapping solution injected for each batch to establish and track typical reagent peak areas. Also document the peak areas of any F-DNPH or other carbonyl-DNPH detected.

### Assembly of Formaldehyde MDTs

Prepare the formaldehyde MDTs as close as possible to the day they will be used. Use clean tubes and caps (see cleaning instructions in Part 6). Each monitoring location requires the preparation of three tubes: two for exposure and one blank. In addition, laboratory MDT blanks have to be prepared. These are MDTs that never leave the laboratory. They are analyzed to determine the batch DNPH amount and batch background F-DNPH as well as any other carbonyl-DNPH amounts. The number of laboratory blanks is at least three, or the square root of the total number of samplers prepared for monitoring.

- 1. Remove the trapping solution from the refrigerator and let it come to room temperature.
- 2. Set out the correct number of red caps in the fume hood on a clean absorbent surface, such as Versi-Dry, a lint-free, superabsorbent barrier layer for laboratory benches. Paper towels can be used, but they will not protect the hood surface in the case of a spill.
- 3. Use tweezers to insert a Whatman Antibiotic Assay Disk (a thick paper filter disk) into each red cap.
- 4. Deliver  $60.0 \mu$ L of the trapping solution by pipettor onto the disks in each cap. Make sure that the solution is distributed evenly over the disks. Use another pipette tip to spread the solution over the disks, if necessary.
- 5. Let the solution dry on the disks in the fume hood for two hours.
- 6. Assemble the formaldehyde MDTs by (1) pushing the colorless cap onto the flat, blunt end of the acrylic tube and (2) pushing the tapered end of the tube into the red cap with the dry filter paper disk.
- 7. Refrigerate the MDTs that will serve as laboratory blanks until you are ready to analyze them. Although this can be done at any time, it is preferable to analyze the laboratory blanks before exposure of the monitoring MDTs so that any problem with the batch can be identified ahead of time.
- 8. Refrigerate the formaldehyde MDTs until you are ready to deploy them.

# Part 4. HPLC Analysis of Samplers Based on DNPH Chemistry

This section describes the protocol used to analyze the formaldehyde MDTs available from the University of Strathclyde as well as commercially available GMD Formaldehyde Dosimeter badges or similarly based 2,4-DNPH PSDs. The protocol is similar to that described by Grzywacz and Tennent (1994).

Carbonyl pollutants in the air are collected on paper tapes (GMD badges) or on filter paper disks (formaldehyde MDTs) impregnated with 2,4-DNPH. The resulting 2,4-dinitrophenylhydrazones that form on the active surface are extracted with acetonitrile and analyzed by reverse-phase HPLC. The system is calibrated with external standards. Identification is made by comparing retention times and UV-Vis spectra of the samples with those of carbonyl-2,4-dinitrophenylhydrazone standards. This application has been very useful for the quantification of carbonyl pollutants in museum environments since the mid-1980s.

# Supplies and Chemicals for Analysis of Samplers Based on DNPH Chemistry Using HPLC

- HPLC grade acetonitrile
- Milli-Q water or HPLC grade water
- 47 mm diameter Zefluor<sup>TM</sup> PTFE Supported Membrane filter, 0.5 μm pore size or similar for organic solvents
- 47 mm diameter PVDF filter, 0.45 μm or Millipore Type HA 47 mm filter, 0.45 μm or similar for aqueous solutions

#### Table A4.2.

HPLC gradient profile for the analysis of DNPH samples

Time	Gradient	% Mobile	Phase A	Description
0 to 8 minutes	None	100%	The first porti 100% A to se F-DNPH, and	on of the analysis is run with parate the DNPH reagent, A-DNPH.
8 to 8.5 minutes	Linear change	Decrease to 30%	Increase the a increasing the	amount of acetonitrile by e percentage of mobile phase B.
8.5 to 12 minutes	None	30%	The higher m dinitrophenyll pushed throu	olecular weight carbonyl-2,4- hydrazone products will be gh the column more quickly.
12 to 12.5 minutes	Linear	Increase to 100%	After all DNP off the colum	H derivatives have been washed n, return to starting conditions.
12.5 to 16 minutes	None	100%	Establish colu Check for flat	mn and system equilibrium. baseline before next analysis.

- C18 Nova Pak<sup>™</sup> 3 mm guard column inserts
- Waters<sup>®</sup> Resolve 5 μm spherical C18 3.9 mm × 15 cm stainless steel column

### Instrumentation

A Waters vacuum system degases mobile phase A (45:55 v/v% acetonitrile:water) and mobile phase B (100% acetonitrile) before they reach two Waters 510 dual-head piston pumps. The flow rate is 1.2 mL·minute<sup>-1</sup>, see table A4.2 for the gradient profile. A 2 µm precolumn stainless steel frit is installed between the pumps and the Waters 717 autosampler to remove debris from shedding pump seals, which is a common problem with acetonitrile mobile phase and rubber seals. In front of the analytical column, there is another in-line 2 µm stainless steel frit precolumn filter and a Waters C18 Nova-Pak<sup>®</sup> 3 mm guard column to remove any particles or contaminates that could harm the analytical column. The sample is separated on a Waters Nova-Pak<sup>®</sup> 4 µm spherical C18 3.9 mm × 150 mm stainless steel column. The analytes are detected with UV-Vis detection using a Waters 996 PDA detector.

All injections are 20  $\mu$ L. Data are collected, stored, and integrated with Waters Millennium software on a PC computer. The chromatogram is extracted at 365 nm for the DNPH derivatives of aliphatic carbonyls.<sup>2</sup>

Gradient elution is used to decrease the analysis time. Many carbonyl compounds are trapped with DNPH samplers. Typically, we are only interested in documenting the peak area of the unreacted 2,4-DNPH reagent and quantifying formaldehyde and perhaps acetaldehyde. These elute within the first few minutes of the analysis, depending on the system, mobile phase strength, and flow rate. The presence of higher molecular weight carbonyl compounds is generally only of qualitative interest, and the system is not calibrated for these compounds. However, they must be removed from the column prior to analysis of subsequent samples. This is expedited with a gradient elution.<sup>3</sup>

### **HPLC Mobile Phase Preparation**

Mobile phase A: 45:55 v/v % Acetonitrile-Water

- 1. Vacuum filter and degas HPLC grade acetonitrile with Zefluor<sup>™</sup> PTFE Supported Membrane 47 mm diameter filter, 0.5 μm pore size or similar.
- Pour 450 mL of the filtered acetonitrile into a 1000 mL graduated cylinder and fill to the 1000 mL mark with Milli-Q water. Note: Milli-Q water is already filtered. If you are using HPLC grade water, it must be filtered before adding it to the filtered acetonitrile. Filter with Millipore Type HA 47 mm filter, 0.45 µm pore size.
- 3. Stopper the graduated cylinder and gently mix together.
- 4. Transfer the 45:55 v/v% acetonitrile-water to mobile phase bottle A.

### Mobile phase B:

- 1. Filter HPLC grade acetonitrile.
- 2. Add to mobile phase bottle B.

### Preparation of Calibration Standards

#### Supplies and chemicals

- Cerilliant Corporation Aldehyde/Ketone-DNPH Standard-13 mixture or individual aldehyde-DNPH standards, e.g., formaldehyde-DNPH and acetaldehyde-DNPH
- Pall<sup>®</sup> Life Sciences LC Minispike Acrodisc<sup>®</sup> 13 mm syringe filters, 0.2 μm pore-size PTFE membrane
- Waters autosampler supplies: 4 mL vials, self-sealing cap assemblies, limited volume inserts and springs

Nine 300 µL standard solutions can be prepared from one ampoule of Cerilliant Corporation Aldehyde/Ketone-DNPH Standard-13 mixture. Table A4.3 lists a suggested 9 standard series that covers the analytical range needed for most DNPH samplers.

- Filter 10 mL HPLC grade acetonitrile using LC Minispike Acrodisc<sup>®</sup> 13 mm syringe filters, 0.2 μm pore size PTFE Membrane to prepare the calibration standards. See filtering instructions in Part 6.
- 2. Use a pipettor to deliver the amount of the aldehyde/ketone-DNPH standard into each vial insert along with the corresponding amount of filtered acetonitrile (see table A4.3). Note: You can mix the standard mixture and acetonitrile and then filter the calibration solution, but there will always be some retention in the syringe filter and you will lose sample.
- 3. Cap each vial and gently mix.

# Preparation of Check Standard

After preparing the 9 calibration standards, there should be more than  $300 \ \mu L$  of the aldehyde/ketone-DNPH Standard-13 remaining. Use this to prepare a check standard that will be used to check the performance of the analytical system at least daily. Table A4.3 recommends a 1:5 dilution

#### Table A4.3.

Suggested preparation of calibration standards using Cerilliant Corporation 1.2 mL ampoule of Aldehyde/Ketone-DNPH Standard-13 mixture in acetonitrile. The concentration of each analyte in the mixture is 15  $\mu$ g·mL-1 aldehyde or ketone per mL.\*

Standard Number	Final Concentration in µg⋅mL <sup>-1</sup>	n µL DNPH Standard	µL Filtered Acetonitrile	Dilution Ratio
Std 1	0.0	0	300	0:1
Std 2	0.3	6	294	1:49
Std 3	0.6	12	288	1:24
Std 4	1.0	20	280	1:14
Std 5	2.5	50	250	1:5
Std 6	5.0	100	200	1:2
Std 7	7.5	150	150	1:1
Std 8	10	200	100	2:1
Std 9	15	300	0	1:0
Total volume of ampoule used: 838 μL of 1200 μL.				
Check Standard	2.5 µg∙mL-1	200 µL	1000 μL	1:5
*Note: This is the concentration of the aldehyde, not the aldehyde-DNPH. If the standard were $\mu$ g·mL <sup>-1</sup> formalde- hyde-DNPH, then it would be necessary to convert the concentration to $\mu$ g·mL <sup>-1</sup> formaldehyde using the ratio of the molecular weights of formaldehyde to F-DNPH, where $C_{\text{complicative}} = \text{CF-DNPH} \times 30.03 \div 210.21$ .				

of the standard with filtered acetonitrile; this will prepare a concentration of 2.5  $\mu$ g·mL<sup>-1</sup>. Store the check standard in the refrigerator.

#### Calibration

Analyze the room temperature calibration standards with the method described above. Inject 20  $\mu$ L of each analytical standard, from dilute to concentrated. Run replicate analyses of 3 or 4 of the 9 standards.

- 1. Integrate each analytical peak of interest, usually only F-DNPH and perhaps Acetaldehyde-DNPH (A-DNPH).
- 2. Record the retention time and peak area at each concentration.
- 3. Save the UV-Vis spectrum of each calibration standard into a library; most chromatographic software has this capability.
- 4. Prepare a calibration chart for each analyte of interest; plot peak area by concentration and use a linear regression fit. Do not force the line through zero. The R<sup>2</sup> for linear regression should be 0.99 or better. Document the equation of the calibration line and R<sup>2</sup>. File the calibration summary with chromatograms of the standards.
- 5. Store the calibration standards in the refrigerator. If they have been analyzed, the septum of each cap will have been pierced. Replace the caps and septa prior to storage.

# Sample Preparation

*GMD Formaldehyde Dosimeter Badges:* GMD Badges have a strip of paper tape impregnated with DNPH. Half of the tape is under the diffusion barrier and is exposed. The other half is protected from exposure and is the in situ blank. Preparation of each GMD badge will generate two samples for analysis: the exposed sample and is the in situ blank sample.

*Formaldehyde MDTs:* Three tubes are used per location sampled: two exposed and one blank. Each tube contains a DNPH-impregnated paper disk for analysis.

# **Chemicals and Supplies**

- HPLC grade acetonitrile
- Pasteur pipets with bulbs
- pipettor and tips
- clean tweezers or forceps—metal or plastic
- clean scissors, preferably only used for GMD badge analysis
- 4 mL vials, 10 mL beakers
- an ultrasonic bath
- 5 mL disposable syringes (Aldrich)
- LC Minispike Acrodisc<sup>®</sup> 13 mm syringe filters, 0.2 μm pore-size PTFE membrane
- Autosampler vials with cap and septum assemblies

Prepare only the samples that can be analyzed the same day.

- 1. Remove the PSDs from the refrigerator and allow them to warm to room temperature. (Remove GMD Badges from their foil storage bag and dispose of the bag and scavenger as hazardous waste.)
- 2. Note the sampling location, badge number, and exposure times in the laboratory notebook. Also, when possible, remove the badge label from the PSD and tape it into the laboratory notebook.
- 3. Label vials with sample location, site ID, and/or badge number. Add an S or a B to designate sample or blank.
- 4. Remove the DNPH-impregnated active surfaces from the samplers as follows:

GMD Badges: Bend the badge to pop up the entire top portion of the badge, exposing the paper tape. Good laboratory practice, specifically, wearing the appropriate personal protective equipment, will ensure that you do not handle the filter paper with your hands-wear gloves and use clean tweezers. The portion of the paper tape with the indented hole is the blank. Hold the blank portion of the tape with clean dry tweezers or forceps. Note: To minimize contamination of the blank from the sample half of the tape, the blank half is held with the tweezers and prepared first. Carefully cut the paper tape in half with scissors. The cut should be made in the middle of the embossed line that divides the blank side from the sample side. It is better to cut more tape for the sample than for the blank; this prevents contamination of the blank. While still holding the blank with the tweezers, carefully place it in the vial labeled "B." Pick up the sample portion of the DNPH paper tape with clean tweezers and place it in the vial labeled "S." To each vial, add 3.00 mL HPLC grade acetonitrile by pipettor to extract the analytes from the filter paper. Rinse the scissor blades and tweezers with acetonitrile to clean for use with the next sampler.

*Formaldehyde MDTs:* Remove the red cap from the tube. Carefully lift the DNPH-impregnated filter paper disk from the red cap with forceps

and place in a labeled 10 mL beaker or bend it to fit into a labeled 4 mL vial. Add 2.0 mL acetonitrile by pipettor to the beaker or vial to wash the sample from the disk. Make sure the entire disk is covered with acetonitrile.

- 5. Sonicate the vial or beaker for one minute.
- Filter the sample with a LC Minispike Acrodisc<sup>®</sup> 13 mm syringe filters, 0.2 μm pore-size PTFE membrane into a clean autosampler vial as described in Part 6. Cap the vial; the sample is now ready to be analyzed.

Repeat the above steps until all samples and blanks are prepared.

Run the samples the same day that they are prepared. If this is not possible, store samples in a refrigerator at approximately 4°C until they can be analyzed.

### Analysis of Samples

If the samples have been stored, remove them from the refrigerator and allow them to warm to room temperature. Equilibrate the HPLC analytical system until the baseline is stable. Analyze a check standard to evaluate the calibration and system performance; that is, calculate retention times, peak areas, and concentrations of target analytes and compare to documented results.

Analyze 20  $\mu$ L of each sample. (Standards and samples should be run with the same injection volumes. This simplifies concentration calculations.) Run replicates of at least every third sample, and run a calibration standard every tenth injection. At the beginning of the day and at the end of the day, run the check standard to confirm the consistency of the results.

Integrate each chromatogram for the analytes of interest. Once the software integration parameters are set up, the automatic integration program is usually satisfactory.

Quantify for each analyte of interest using the calibration acquired above. Calibrations can remain consistent up to several weeks. The check standard is useful for tracking the stability of the calibration with respect to retention time, peak area, and calculated concentration.

Laboratory Blanks Formaldehyde MDTs: Document the peak area (PA in calculation examples) of the 2,4-DNPH reagent peak. This is useful to measure the consistency of PSD preparation. There should be no formaldehyde-2,4-dinitrophenylhydrazone (F-DNPH) or other carbonyl-DNPH peaks detected in the laboratory blanks. If there is contamination, document the peak areas for each analyte observed on the blanks.

GMD Blanks and Formaldehyde MDTs Sampling Blanks: Document the peak area of the 2,4-DNPH reagent peak. This is useful to measure the consistency of PSD preparation. It will also be used to determine any breakthrough for the GMD badges or overexposure of the MDTs. Document the peak area of any carbonyl -DNPHs, if present.

*Samplers:* Document the peak area of the 2,4-DNPH excess reagent peak, the peak areas of the analytes, and the calculated concentration of each

analytical peak of interest, usually only formaldehyde. Print each chromatogram and a report of retention time, peak height, peak area, and concentration based on calibration files.

After analysis, replace the pierced septa on the autosampler vials with new cap assemblies, and store the vials in a refrigerator at approximately 4°C. Samples can be reanalyzed within a month of preparation. Gibson and Brokerhof (2001) found that samples were stable for thirty-five days after preparation.

# Calculating Formaldehyde Concentrations<sup>4</sup>

1. Document the peak area of the 2,4-DNPH reagent for samples and blanks.

The results arrived at in this step will be used in Part 5 to evaluate confidence of the results.

Document the 2,4-DNPH reagent peak area for the blanks:

GMD blank (PA<sub>DNPH GMD-Blank</sub>)

Formaldehyde MDT laboratory blanks (PA<sub>DNPH lab-blanks</sub>) – samplers prepared and stored in the laboratory. *Calculate the average and standard deviation for the laboratory blanks, then use this average in Part 5.* 

Formaldehyde MDT location blank ( $PA_{DNPH \ blank-tube}$ ) – samplers taken to the monitoring location but not exposed. Use this number if you do not have the information for the MDT laboratory blanks.

*Note:* The average  $PA_{DNPH \ lab-blanks}$  and  $PA_{DNPH \ blank-tube}$  should be the same within the standard deviation of the laboratory blanks. If they are not, it is an anomaly with the location set of samplers and should be documented.

Document the peak area for the residual 2,4-DNPH detected on the exposed samplers: GMD badges (PA<sub>residual DNPH GMD</sub>)

Formaldehyde MDTs (PA<sub>residual DNPH-tube 1</sub> and PA<sub>residual DNPH-tube 2</sub>)

2. Calculate the sample concentration in  $\mu g \cdot mL^{-1}$ . If your chromatographic software reports sample concentration in  $\mu g \cdot mL^{-1}$  directly, skip to Step 3.

If your software only reports peak area, you will have to generate a calibration curve by plotting peak area versus concentration. Use the basic linear calibration equation Y = mX + b to calculate the concentration of the sample ( $C_{sample}$ ), where Y = PA; m = slope;  $X = C_{sample}$ ; and b = y-intercept.

$$PA = (slope) \times C_{sample} + y-intercept$$

Solving for the concentration  $(C_{sample})$  yields the amount (µg) of formaldehyde detected per mL of sample.

It is important to adjust  $C_{sample}$  for any difference between the injection volume of the sample and the injection volume of the calibration standards.

 Calculate the net or blank corrected concentration (C<sub>net</sub>) in µg⋅mL<sup>-1</sup> for each sample.
 CMD he does To obtain C

*GMD badges:* To obtain  $C_{GMD-net}$ , subtract the concentration detected on the blank half of the paper tape ( $C_{GMD-blank}$ ) from the concentration calculated on the sample half of the tape ( $C_{GMD-sample}$ ).

$$C_{GMD-sample} - C_{GMD-blank} = C_{GMD-net}$$

If  $C_{GMD-blank}$  is greater than  $C_{GMD-sample}$ , the result will be a negative number. This should be reported as less than the detection limit and the detection limit should be stated in the report.

Formaldehyde MDT laboratory blanks: No F-DNPH should be detected on the laboratory blanks. If there is, calculate the average concentration and subtract  $C_{lab-blank}$  from the concentrations detected on each of the three deployed tubes ( $C_{tube-1}$ ,  $C_{tube-2}$ ,  $C_{blank-tube}$ ) to obtain the laboratory blank-adjusted concentrations.

$$C_{tube-1} - C_{lab-blank} = C_{tube-1 adj}$$
$$C_{tube-2} - C_{lab-blank} = C_{tube-2 adj}$$
$$C_{blank-tube} - C_{lab-blank} = C_{blank-tube adj}$$

*Formaldehyde MDTs:* Three MDTs are used per location: two are exposed, and the third is a blank. To obtain net concentration ( $C_{tube-1-net}$ ,  $C_{tube-2-net}$ ), subtract the concentration of the location blank ( $C_{blank-tube}$ ) from concentration observed for both of the exposed tubes,  $C_{tube-1}$  and  $C_{tube-2}$ . Use concentrations adjusted for laboratory blanks if necessary.

$$C_{tube-1} - C_{blank-tube} = C_{tube-1-net}$$
  
 $C_{tube-2} - C_{blank-tube} = C_{tube-2-net}$ 

If  $C_{blank-tube}$  is greater than  $C_{tube-2}$  or  $C_{tube-1}$ , the result will be a negative number. This should be reported as zero and or as less than the detection limit.

4. Determine amount of trapped formaldehyde on the sampler. We have calculated the net concentration  $C_{net}$  ( $C_{GMD-net}$  or  $C_{tube-1-net}$  and  $C_{tube-2-net}$ ) per mL of sample. Now we need to determine the amount of pollutant trapped on the sampler. For this, we need the volume of ace-tonitrile used to extract or wash the DNPH analytes ( $V_{wash}$ ) from the active surface.
#### Appendix 4

Multiply the  $C_{net}$  in  $\mu g \cdot m L^{-1}$  by the  $V_{wash}$  in mLs per sampler. This will yield  $\mu g$  formaldehyde trapped on the sampler  $C_{trapped formaldehyde}$  or  $C_{formaldehyde}$ 

$$C_{net} (\mu g \cdot mL^{-1}) \times V_{wash} (mL) = C_{trapped formaldehyde} (\mu g)$$

where the wash volume for GMD badges = 3.00 mL, and the wash volume for formaldehyde MDTs = 2.00 mL.

Now we have the amount in  $\mu g$  of pollutant trapped on the PSD. To be of use in evaluating pollutant levels in museums, this amount must be converted to  $\mu g \cdot m^{-3}$  and, ultimately, to ppb. Steps 5 and 6 take you through this process.

### 5. Determine volume of sampled air.

The first step in arriving at pollutant concentrations in ppb is calculating the volume of air ( $V_{air}$ ) that diffused through to the sampler's active surface. Multiply the PSD's exposure time in minutes ( $T_{exp}$ ) by the device's sampling rate (SR). Sampling rates are listed in table A4.1 (if you are interested in quantifying the amount acetaldehyde with the GMD Formaldehyde Dosimeter badge, the sampling rate is also listed). This gives the volume in mL. Multiply by  $10^{-6}$  m<sup>3</sup>·mL<sup>-1</sup> to obtain the volume in cubic meters.

$$T_{exp} \times SR \times 10^{-6} \text{ m}^3 \cdot \text{mL}^{-1} = V_{air} \text{ in } \text{m}^3$$

For a GMD badge exposed for 2 days, 8 hours, and 15 minutes (3375 minutes) with a formal dehyde sampling rate of 25.2 mL·min<sup>-1</sup>, the V<sub>air</sub> calculation is

$$V_{air} = 3375 \text{ min} \times 25.2 \text{ mL} \cdot \text{min}^{-1} \times 10^{-6} \text{ m}^3 \cdot \text{mL}^{-1} = 0.85 \text{ m}^3$$

6. Determine pollutant concentration in  $\mu g \cdot m$ -3 and convert it to ppb. Divide the  $\mu g$  of trapped formaldehyde per sampler arrived at in Step 4, by the m<sup>3</sup> volume of air sampled (V<sub>air</sub>) arrived at in Step 5. This calculation yields the amount of pollutant per cubic meter of air (C<sub>formaldehyde air</sub>) for each location.

 $C_{trapped formaldehyde} \div V_{air} = C_{formaldehyde air}$ 

For 5.6 µg formaldehyde detected on a GMD badge with  $V_{air} = 0.085 \text{ m}^3$ , the pollutant concentration in air is

5.6 
$$\mu$$
g ÷ 0.085 m<sup>3</sup> = 66  $\mu$ g·m<sup>-3</sup>

Use the conversion factor in table 3.1 or the online concentration converter (http://www.iaq.dk/papers/conc-calc.htm) to convert  $\mu g \cdot m^{-3}$  to ppb at 20°C and 1 atm (this is STP as defined by the Compressed Air and Gas Institute; see chap. 3).

Using the conversion factor for formaldehyde found in table 3.1, the above example becomes

66 μg·m<sup>-3</sup> formaldehyde × 0.80 ppb/μg·m<sup>-3</sup> = 53 ppb formaldehyde

If you are measuring the concentrations with formaldehyde MDTs, calculate the concentration detected on each tube, then report the average of the two tubes.

### Part 5. Determination of Sampler Overexposure or Analyte Breakthrough

For GMD Formaldehyde Dosimeter badges, if analyte is detected on the blank portion of the active surface (paper tape), this indicates that the exposed portion became sufficiently depleted (not necessarily completely depleted) and breakthrough occurred. The results are not accurate. This would also be true for other DNPH-based devices with in situ blanks, such as the SKC UMEx 100<sup>™</sup> Passive Sampler. Determining overexposure for other devices such as the formaldehyde MDTs is not as straightforward.

Quantitative chemical reactions require an excess of reagent. The pollutant should be the limiting reagent, not the trapping chemical. Each time a pollutant molecule reaches the active surface, it should react with the trapping reagent. As the reagent is used up and the sampler becomes loaded with pollutant, there is less trapping reagent to react with additional pollutant. This is because the remaining trapping reagent is now located deeper into the active surface and is not as available. In this case, the effective reagent amount becomes depleted, and the true pollutant concentration in the air would be greater than the calculated concentration.

By calculating the percent of residual reagent left on DNPH samplers, we can estimate the reliability of the results. This is feasible with DNPH chemistry because the reagent is observed by the analytical method. This cannot be done for the KOH MDTs because analysis does not detect the reagent, only the trapped pollutants.

#### Calculating Percent of Residual Reagent Left on DNPH Samplers

Use the data documented in Step 1 of "Calculating Formaldehyde Concentrations."

1. GMD Formaldehyde Dosimeter badges Calculate residual reagent as follows:

% residual DNPH = ( $PA_{residual DNPH GMD} \div PA_{DNPH GMD-Blank}$ ) × 100

where  $PA_{residual DNPH GMD}$  = the reagent DNPH peak area for the sample portion of the tape, and  $PA_{DNPH GMD-Blank}$  = the reagent DNPH peak area for the blank portion of the paper tape.

2. Formaldehyde MDTs Calculate residual reagent as follows:

#### Appendix 4

% residual DNPH =  $(PA_{residual DNPH-tube 1} \div PA_{DNPH lab-blanks}) \times 100$ 

where  $PA_{residual DNPH-tube 1}$  = the reagent DNPH peak area for sample tube 1, and  $PA_{DNPH \ lab-blanks}$  = the average reagent DNPH peak area for the MDT laboratory blanks ( $PA_{DNPH \ blank-tube}$ , the reagent DNPH peak area for the MDT location blank, can also be used).

Repeat this calculation for sample tube 2 and average the results to report % residual DNPH for the location.

Based on the experience of the GCI laboratory, we developed the following guidelines to determine reliability of results from DNPH samplers:

- If residual DNPH is greater than 80%, the results are acceptable.
- If between 70% and 80%, the results are questionable.
- If less than 70%, the results are unacceptable, and the exposure(s) should be repeated.

# Part 6. Techniques

# Filtering Analytical Samples for HPIc or ic Analysis

- 1. Remove the plunger from a 5 mL disposable syringe.
- 2. Attach the appropriate 13 mm Acrodisc<sup>®</sup> syringe filter to the barrel of the 5 mL disposable syringe.
- 3. Transfer the sample into the syringe barrel with a glass Pasteur pipet; deliver the sample into the nib of syringe barrel to reduce air bubbles and maximize sample recovery.
- 4. Insert the plunger and slowly push the plunger to filter the analytical sample into a prelabeled autosampler vial. Note: If you push too hard or too quickly, the force can separate the filter slightly from the syringe or even break the filter membrane. Either case results in a loss of sample.

Do not reuse the syringe or filter. Properly dispose of both as hazardous waste.

# Preparing Twice-Recrystallized 2,4-DNPH

Supplies and Chemicals

- 2,4-dinitrophenylhydrazine (2, 4-DNPH)
- ethanol
- Whatman Laboratory Product Grade No. 1 filter paper
- Kimberly-Clark<sup>®</sup> Kaydry<sup>®</sup> EX-L 2-ply wipes

# Preparation

- 1. In a 500 mL Erlenmeyer flask, dissolve 2 g of 2,4-DNPH in 200 mL of warm ethanol, approximately 50°C.
- 2. Filter through a Büchner filter funnel into a 500 mL filter flask. Rinse with chilled ethanol.

- 3. Refrigerate the filtrate and allow it to recrystallize.
- 4. Collect the 2,4-DNPH crystals by suction using a Büchner filter and rinse with chilled ethanol.
- 5. Repeat Steps 1-4.
- 6. Finally, collect the twice-recrystallized 2,4-DNPH.

# Cleaning MDTs: Tubes, Caps, and Stainless Steel Meshes

Place the tubes, caps, and stainless steel meshes in a large glass container (e.g., 1 L beaker) along with a non-ionic soap such as Micro-90<sup>®</sup> Concentrated Cleaning Solution (VWR International Scientific). Let stand overnight.

- Rinse container, tubes, caps, and meshes thoroughly with tap water to remove all traces of the soap.
- Rinse the tubes, caps, and meshes in the container twice with Milli-Q water. Fill with Milli-Q water and leave the tubes, caps, and meshes to soak overnight.
- Remove the tubes, caps, and meshes from the container and set on Kaydry<sup>®</sup> EX-L wipes to absorb excess water.
- To completely dry the tubes and caps, place them in a dessicator containing dry silica gel. These items may be stored in the dessicator until they are needed.
- To dry the stainless steel meshes, place them between two Kaydry<sup>®</sup> EX-L wipes. Store in a sealed plastic bag.

## Notes

- 1. Milli-Q water specifications: 18.2 M $\Omega$ ·cm resistivity at 25°C with low (1–5 ppb) total organic compounds filtered with 0.22 µm pore-size Milli-Pak<sup>®</sup> filter unit.
- 2. If conjugated carbonyl compounds are of interest, it is useful to extract the chromatogram at higher wavenumber.
- 3. The same procedures are used to calculate the concentrations of other aldehydes or ketones.
- 4. If desired, the gradient profile can be modified to achieve full separation of all DNPH derivatives. However, this will increase the analysis time from 15 minutes to over 40 minutes. If you are interested only in identifying other carbonyl compounds, it is not necessary to perform a full calibration for each compound. Relative peak heights or peak areas can be used to estimate concentrations.

## Materials and Suppliers

*Note:* See addresses of suppliers following this list. Acetonitrile, HPLC grade

J. T. Baker Analytical JT9017 or similar VWR International Scientific

#### Appendix 4

C18 Nova-Pak<sup>®</sup> 3 mm guard column inserts Waters Corporation

C18 Nova-Pak<sup>®</sup> 4  $\mu$ m spherical 3.9 mm  $\times$  15 cm stainless steel column Waters Corporation

2,4-dinitrophenylhydrazine D199303 Sigma-Aldrich Corp.

2,4-dinitrophenylhydrazine: Twice recrystallized PN ERD-010 Cerilliant Corporation

## Disposable syringes 5-mL

All polypropylene/polyethylene, sterilized Aldrich Z11686-6 Sigma-Aldrich Corp.

# **DNPH Standards:**

Aldehyde/Ketone-DNPH Standard-13 mixture Cerilliant Corporation ERA-028 Or individual aldehyde-DNPH standards formaldehyde-DNPH, 10 mg Cerilliant Corporation ERF-003 acetaldehyde-DNPH, 10 mg Cerilliant Corporation ERA-012

# Ethanol, reagent-grade or HPLC grade

Burdick and Jackson BJAH90 or similar VWR International Scientific

Ethylene glycol dimethyl ether, 99.9%, HPLC grade Aldrich 30743-2 Sigma-Aldrich Corp.

# Ion Chromatography Acrodisc<sup>®</sup> 13 mm syringe filters

0.2 μm pore-size Supor<sup>®</sup> membrane Pall<sup>®</sup> Life Sciences PN 4483

VWR International Scientific PN 28144-030

Kaydry<sup>®</sup> EX-L, Delicate Task Wipers, Kimtech Science<sup>®</sup> 100% virgin fiber, low linting, nonabrasive 12 in. × 12 in., 3-ply Kimberly-Clark<sup>®</sup> PN 34743 VWR International Scientific PN 10805-905

# LC Minispike Acrodisc<sup>®</sup> 13 mm syringe filters

0.2 μm pore-size PTFE membrane Pall<sup>®</sup> Life Sciences PN 4552

VWR International Scientific PN 28143-254

# Micro-90<sup>®</sup> Concentrated Cleaning Solution PN 21830-416

**VWR** International Scientific

# Millipore Type HA (mixed cellulose esters) 47 mm filter 0.45 μm pore size Millipore Corp.

Milli-Q<sup>®</sup> Filtration System Millipore Corp.

# Orthophosphoric acid - concentrated, 85%

Mallinckroft Analytical, MK279618 VWR International Scientific

# Palmes Open-Path Diffusion Tube Assembly

- clear polymethylmethyacrylate tubes (7.1 cm  $\times$  1.1 cm) #DIF 100
- acrylic clear caps, used to seal the blunt open end #DIF CAP-001
- acrylic red caps, used for tapered closed end of aldehyde tubes #DIF CAP-002
- acrylic blue caps, used for tapered closed end of acid tubes #DIF CAP-003
- stainless steel mesh #DISC

Gradko International Ltd.

# Potassium Hydroxide Pellets

Aldrich #30656-8 Sigma-Aldrich Corp.

# PVDF membrane 47 mm diameter filter 0.45 µm pore size

Pall<sup>®</sup> Life Sciences VWR International Scientific

Sodium acetate (acetic acid sodium salt) Aldrich 229873 Sigma-Aldrich Corp.

#### Appendix 4

Sodium formate (formic acid sodium salt) Aldrich 456020 Sigma-Aldrich Corp.

Sodium tetraborate decahydrate, ACS reagent grade 99.5–105.0 Sigma S9640 Sigma-Aldrich Corp.

Versi-Dry, super-absorbent barrier layer for laboratory benches VWR International Scientific

## Waters Autosampler Supplies

- 4 mL vials with cap and septa (PN 186000838)
- self-sealing cap assemblies (PN PSL410408)
- limited volume insert (LVI) (PN WAT072704)
- springs for LVI (PN WAT072708)

Waters Corporation

# Whatman® Laboratory Products: Antibiotic Assay Disks

Grade AA, 0.2 mm pore size, 1.1 cm diameter. PN 2017013, special order from VWR International Scientific

# Whatman Laboratory Products: Grade No. 1 filter paper VWR International Scientific

# Zefluor™ PTFE Supported Membrane, 47 mm diameter filter 0.5 µm

pore size Pall<sup>®</sup> Life Sciences PN P5PQ047 VWR International Scientific PN 28139-583

# Addresses

Cerilliant Corporation www.cerilliant.com 811 Paloma Dr., Ste A Round Rock, TX 78664 USA Telephone: 1-800-848-7837 U.S. and Canada 512-238-9974 International Fax: 1-800-654-1458 U.S. and Canada (512) 238-9129 International

Gradko International Ltd. www.gradko.co.uk St. Martins House, 77 Wales St. Winchester Hampshire SO23 0RH United Kingdom Telephone: +44 (0) 1962 860331 Fax: +44 (0) 1962 841339

Millipore Corp. www.millipore.com 290 Concord Rd. Billerica, MA 01821 Telephone: 978-715-4321 / 1-800-645-5476 Fax: 1-800-645-5439

Pall® Life Sciences 2200 Northern Blvd. East Hills, NY 11548 Telephone: 516-484-5400 / 1-800-645-6532 Fax: 516-484-5228

Sigma-Aldrich Corp. www.sigmaaldrich.com St. Louis, MO Telephone: 314-771-5765 Fax: 314-771-5757

VWR International Scientific www.vwr.com 1310 Goshen Pkwy West Chester, PA 19380 Orders: 1-800-932-5000

Waters Corporation www.waters.com 34 Maple St. Milford, MA 01757-3696 Telephone: 1-800-252-HPLC

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## PAGE 13

Figure 2.2. Photos by Davina Graham. Courtesy of Glasgow City Council (Museums), The Burrell Collection. © CSG CIC Glasgow Museums Collection.

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Figures 2.3b and 2.3c. Model of the battle of Waterloo. British, 1842-3. Made by Captain William Siborne (XVIII.82). Images by Barry Knight. Reproduced by kind permission of the Royal Armouries Museum.

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Figure 2.4. Photos by Davina Graham. Courtesy of Glasgow City Council (Museums), The Burrell Collection. © CSG CIC Glasgow Museums Collection.

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Figures 2.7a and 2.7b. Photos by Davina Graham. Courtesy of Glasgow City Council (Museums), The Burrell Collection. © CSG CIC Glasgow Museums Collection.

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Table 4.3. Bio-Check-F badge and Bio-Check-Ozone badge © Drägerwork AG & Co. KGaA, Lubeck. All rights reserved. No portion hereof may be reproduced, saved or stored in a data processing system, electronically or mechanically copied or otherwise recorded by any other means without our express prior written permission.

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Table 4.3. The correct telephone number for Vistanomics, Inc. is 888-782-9992.

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Table A4.1. The sampling rates for formic acid and acetic acid were inadvertently switched.Row 4 should read: "formic acid 1.02 mLmin-1"Row 5 should read: "acetic acid 0.88mLmin-1"