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Source: *Objects Specialty Group Postprints, Volume One, 1991*
Pages: 33-41
Compiler: Pamela Hatchfield

PASSIVE MONITORS FOR THE DETECTION OF POLLUTANTS IN MUSEUM ENVIRONMENTS

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ABSTRACT

In recent years there has been much concern about air pollutants in the museum environment. GCI has undertaken an extensive Environmental Research Program quantifying pollutants in the museum environment. Dynamic sampling methods were used to detect low parts per billion (ppb) levels of many of these pollutants. Simple, economical passive monitors have been developed based upon the chemistry used in the dynamic sampling modes. Commercially available monitors and a generic passive sampler are discussed. Some passive samplers can be used for direct reading (no analysis required) determination of a number of pollutants. Validation studies are presented along with applications and use of the passive monitors.

INTRODUCTION

There are a number of problems which can arise when cultural property is stored in an environment with airborne pollutants. Leaded coins have been known to deteriorate when stored in highly acidic environments such as those which may develop in oak storage trays or cabinets. Calcareous materials, such as shells, are also susceptible to attack by pollutants. The development of white and gray efflorescence on shells is termed Byne's Disease (Byne 1899) and has been reported at a number of museums including the Bishop Museum in Honolulu, Hawaii and the Queensland Museum, Brisbane, Australia (Agnew 1981). For several decades, carbonyl compounds and organic acids have been recognized in the museum world as corrosive agents for lead objects, leaded bronzes, ethnographic objects, and a variety of other materials (Nockert and Wadsten 1978; Kamath et al 1985; Tennant and Baird 1985; Padfield et al 1982; Hatchfield and Carpenter 1985).

Sometimes the signs of a potentially dangerous atmosphere can be seen on a storage cabinet's hardware. At one museum, the concentration of airborne pollutants was great enough to corrode the internal lock mechanisms of storage cabinets. Although the cabinets were constructed of high quality laminated plywood, the non-laminated edges were exposed inside the cabinets. This resulted in the emission of damaging levels of corrosive volatile compounds, mainly formaldehyde, from the adhesives used in the manufacturing of the plywood. The first indication of the detrimental environment was the corrosion of the locks. This led to a survey of the collection objects in the cabinets. Upon examination, it was apparent that the

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objects also exhibited problems associated with a corrosive environment, such as the development of white crystalline efflorescence on many Asian metal artifacts.

The sources of formaldehyde in a museum environment may be obvious, such as formalin solutions used in the storage of animal or reptile specimens leaking from improperly sealed vessels, or formaldehyde adhesives used in the manufacture of plywood and particle board. However, it is often difficult to discover whether an environment contains potentially harmful pollutants, as well as to identify what the pollutants are and to pinpoint their sources. Therefore, simple qualitative tests such as the "lead coupon" test have been used to obtain a general sense of whether airborne pollutants are present. The conservator simply exposes a clean strip of lead in the suspect environment. At designated times, the strip is visually examined for the development of a gray-white efflorescence. If such surface corrosion occurs on the lead test strip, the curator or conservator is alerted to the potentially damaging environment and can seek mitigation methods. However, such tests are only an indication of the environment in singular locations, and they do not identify the antagonistic pollutant. Due to the increasing awareness of pollutants in the museum environment, the Getty Conservation Institute (GCI) became interested in going beyond this simple pollution indicator test and in finding a way to quantitate levels of formaldehyde an other carbonyl compounds.

Environmental Research Program

GCI's Environmental Research Program developed a five point strategy for pollutant control:

- Develop an *analytical method* capable of detecting the levels of specific classes of pollutants found in museum environments.
- Conduct a *survey* to determine the baseline levels of pollutants.
- Determine *material damage functions*. At what pollutant concentration does detectable damage occur on organic and inorganic materials.
- Identify or develop economical *passive sampling devices*.
- Discover and validate *mitigation methods and technologies*.

The first two objectives for formaldehyde have been completed (C. Druzik and Taketomo 1988; C. Druzik et al 1990), the materials damage research has been reported (Striegel 1991), the mitigation research is work in progress and the passive sampling devices are the subject of this paper.

Background Research: Survey of Indoor-Generated Airborne Carbonyl Pollutants

In the late 1980's, GCI conducted a survey of airborne carbonyl pollutants at 17 participating institutions from the East Coast to the West Coast, including Hawaii. Nearly six hundred air samples were collected from almost 200 sites within these institutions. This survey provided important baseline pollutant-concentration data for formaldehyde, acetaldehyde, formic acid and acetic acid. The emphasis of this paper is on formaldehyde which was the most prevalent airborne pollutant detected.

Before reviewing the results of the museum survey of indoor generated airborne carbonyl pollutants the following reference levels should be considered:

> In a typical US home of wood and particle board construction with no urea-formaldehyde foam insulation the typical concentration of formaldehyde is 30 parts per billion (Gammage and Hawthorne 1985).
>
> The outdoor concentration of carbonyl pollutants depends on climate and weather conditions. For Southern California, where the majority of the participating institutions were located, the outdoor ambient carbonyl concentrations are in the low ppb range (Grosjean and Fung 1984, Grosjean 1988, 1991):

formaldehyde:	1-29 ppb
acetaldehyde:	1-13 ppb
formic acid:	1-8 ppb
acetic acid:	2-10 ppb

> As a reference for "clean air" or an ultimate baseline level, consider the concentration of formaldehyde detected in the troposphere, 0.4 ppb (Seinfeld 1986) and the concentration of carboxylic acids detected in arctic air, 0.1 ppb (Talbot et al 1988).

The concentration range of formaldehyde detected at the seventeen participating institutions was from less than 0.2 parts per billion (the detection limit of the analytical method) to 1400 parts per billion (ppb). A summary of the survey statistics can be found in Table 1, and the distribution of carbonyl concentrations detected is presented in Table 2. The median concentrations of carbonyl pollutants was 6-12 ppb. Examination of the distribution of pollutant concentrations revealed that the majority of the sites sampled had concentration less than 50 ppb, only 10-15% of the sites sampled had concentrations greater than 50 ppb. Furthermore, the majority of the samples with "high" (>50 ppb) concentrations of formaldehyde were from areas with little air circulation, such as inside display cases and storage cabinets, and all locations with concentration in excess of 100 ppb were display cases or storage cases. This is not to say, however, that all display cases and storage cabinets had high levels of formaldehyde or other carbonyl pollutants; that would make our task too easy!

TABLE 1: Survey Statistics:
GCI Survey of Indoor-Generated Carbonyl Pollutants

	Formaldehyde	*Formic Acid*	*Acetaldehyde*	*Acetic Acid*
Median	12	6	8	10
Mean	42	14	23	32
Minimum	<0.2	<0.3	<0.2	<0.5
Maximum	1400	290	850	1600

TABLE 2: Distribution of Concentrations:
GCI Survey of Indoor-Generated Carbonyl Pollutants

Concentration Range (ppb)	*Formaldehyde*	*Formic Acid*	*Acetaldehyde*	*Acetic Acid*
< 19	113 (66%)	143 (83%)	137 (80%)	112 (65%)
20-49	33 (20%)	19 (11%)	27 (16%)	35 (20%)
50-99	12 (7%)	6 (3%)	2 (1%)	14 (8%)
100-500	11 (6%)	4 (3%)	4 (2%)	9 (5%)
> 500	3 (2%)	0	2 (1%)	2 (1%)

From the survey, it was learned that formaldehyde is not ubiquitous. In areas where formaldehyde concentration was high, this could be explained as originating in the types of building materials used, the quality of ventilation as well as the age of the site. It is well known that new plywood and particle board manufactured with urea-formaldehyde resins, for example, can produce copious quantities of formaldehyde (Meyer 1979; Grzeskowiak 1988). If the area is not well ventilated, the pollutant concentrations build up. As the material ages, however, emissions decrease.

PASSIVE SAMPLING DEVICES FOR AIRBORNE FORMALDEHYDE

The goal at the outset of the Passive Monitor Project was to identify passive sampling devices (PSDs) which would be used to detect single digit part per billion levels of pollutants or identify passive samplers whose technology could be stretched to achieve the necessary low limits of detection. In the first phase of the project, the emphasis was on evaluating formaldehyde PSDs developed commercially. Not only was the conservation community concerned about formaldehyde, but it was recently added to the State of California's list of carcinogenic compounds. The interest in detection of formaldehyde in the work place was advantageous for our project, as there were a number of products on the market for passive detection of this pollutant.

Among the products explored in our study were Sensidyne and National Draeger detector tubes. Detector tubes are pollutant specific. These sorbent tubes are attached to dedicated manual pumps, and a specified number of air strokes are pulled through the tube. In this way, a known volume of air is sampled, and the pollutant concentration can be directly determined based on a color change of the sorbent and the scale on the tube. These formaldehyde detector tubes were not feasible for use in detecting the low concentrations of formaldehyde seen in the museums; they are designed for measuring much higher levels of formaldehyde. While high ppb levels of formaldehyde in museums could be detected by increasing the number of strokes through the tube, the number of strokes required to detect low concentrations of formaldehyde was impractical.

A number of dosimeter type badges developed in response to OSHA and ASHRAE limits on formaldehyde exposure in the work place were also tested. Like the detector tubes, these monitors were designed for much higher formaldehyde concentrations than were present in museums. The detection limits of these badges were two orders of magnitude greater than formaldehyde concentration typically found in galleries and storage areas. We also looked at 3M-brand™ Formaldehyde Monitor and DuPont's ProTek™ badge, both of which were not sensitive enough. Neither Air Quality Research, Inc.'s PF-12 Formaldehyde Monitor nor the Bacharach AirScan™ formaldehyde exposure monitors were good candidates for use in museum environments due to reproducibility and exposure requirement problems.

Finally, we tested the GMD 570 Series Formaldehyde Dosimeter badge. The initial tests were promising, and a passive sampling device validation protocol was developed. Each potential passive sampler was subjected to the following tests:

- Detection Limits
- Reproducibility
- Percent Recovery
- Comparison with Active Sampling
- Interference Studies
- Effects of Low Air Velocity
- Field Tests

Detection Limits: Because the selection of the passive sampling device was for the measurement of museum environments where the concentration of pollutants may be low, it was necessary to ensure that a potential passive sampling device (PSD) was effective at the desired level, in the range from 5 ppb to 1500 ppb for formaldehyde.

Reproducibility: Reproducibility was confirmed to establish the validity of using a limited number of PSDs (frequently only one) at a particular location.

Percent Recovery: The amount of analyte recovered when the passive sampler was exposed to a known amount of pollutant was determined. A PSD was spiked with a known amount of analyte, and compared to the amount of analyte recovered during the analytical process. This is a measure of the analytical method.

Comparison with Active Sampling: The passive sampling device was compared with a standardized active sampling method to further validate its use.

Interference Studies: The badge's response to the target pollutant in the presence of potential interferences was studied. Because the museum environment consist of many different chemical species, interference studies were conducted to determine any substantial positive or negative interference from other pollutants.

Effects of Low Air Velocity: As noted before, locations with the highest concentrations of pollutants were the sites with little or no air circulation, such as display cases. Hence, the PSD's effectiveness in a sealed case with no air circulation was tested.

Field Tests: Finally, the validated passive monitor was tested in the field at a museum.

The GMD formaldehyde dosimeter badge performed very well in the validation tests completed to date. The detection limit was determined to be 5.6 ppb/hour. This translates to 0.2 ppb for a twenty-four hour exposure. The reproducibility of the badges was found to be 95-98%; i.e., the variance among six GMD badges was only 2-5%. The percent recovery was 99%; all of the analyte added to the badge was recovered. When the badges were compared with the active sampling method, the ratio of the amounts of formaldehyde detected was 1.13; in other words, the badges saw 13% more formaldehyde than was detected by active sampling. The difference in the amount of formaldehyde detected in a still-air case when compared to a case with high air circulation was 20%. While this seems high, the US Environmental Protection Agency allows a 20-30% difference to be a reasonable result when comparing active and passive samplers. The chemistry of the badges is very selective. There were no interferences with typical atmospheric pollutants. Field tests have been successfully completed at three museums.

There are a few cautions when using the GMD badges. The badges must be stored in a freezer, and they should be used within 6 months of purchase. This is beyond the date specified by the manufacturer, but they incorporate a large margin of safety. The badges can be exposed 24-48 hours; with any longer exposure periods, one runs the risk of overexposing the dosimeter badge. The badges should be analyzed within one month after exposure. GMD Systems, Inc. does provide economical analysis; however, they can take a month to report the results. Because of this time delay, the exposed badges should be returned for analysis as soon as possible after exposure. Care must be exercised when placing the badges inside a case or cabinet to maintain the integrity of the internal air quality. One cannot leisurely place the badge inside a cabinet or case, or in a very short time, there will be complete air exchange and dilution of the internal air with room air. Rather, one must open the case minimally and "slip" the badge into the case or cabinet. Fortunately, the badges are very thin, and this is easily achieved. Thus, a GMD dosimeter badge can be used to determine levels of formaldehyde in museum environments.

GMD 570 series formaldehyde dosimeter badges are available from GMD Systems, Inc.; Old Route 519; Hendersonville, PA 15339 USA; (412) 746-3600. The part numbers are 570-010 for the badges only and 570-050 for badges with prepaid analysis, at a cost of $100 per 10 package and $400 per 10 package, respectively (as of June 1991). The badges come with instructions for exposure and storage. There are also explicit analysis instructions for those individuals who have access to an analytical laboratory equipped with a high performance liquid chromatography (HPLC) system.

Future Work

The Passive Monitor Project and the search for mitigation technologies continues. GCI plans to identify or develop passive sampling devices for ozone, nitrogen dioxide, hydrogen sulfide and sulfur dioxide within the next year. With the increasing awareness of indoor air quality, many companies are developing passive sampling devices for these pollutants. It is hoped that we will be able to recommend direct-reading passive samplers or samplers that require no special analysis, much like litmus paper for the testing of pH.

Acknowledgements

The authors would like to acknowledge Daniel Grosjean and Associates for technical contributions to the validation of the GMD passive sampler, Karen Cole for her technical assistance and Karen Sexton-Josephs for her assistance in the preparation of this paper.

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