Narrative Section of a Successful Application

The attached document contains the grant narrative of a previously funded grant application. It is not intended to serve as a model, but to give you a sense of how a successful application may be crafted. Every successful application is different, and each applicant is urged to prepare a proposal that reflects its unique project and aspirations. Prospective applicants should consult the NEH Division of Preservation and Access application guidelines at http://www.neh.gov/divisions/preservation for instructions. Applicants are also strongly encouraged to consult with the NEH Division of Preservation and Access staff well before a grant deadline.

Note: The attachment only contains the grant narrative, not the entire funded application. In addition, certain portions may have been redacted to protect the privacy interests of an individual and/or to protect confidential commercial and financial information and/or to protect copyrighted materials.

Project Title: Rapid Pollution Off-Gassing Assessments of Museum Construction
                Materials by Gas Chromatographic

Institution: Indianapolis Museum of Art Techniques

Project Director: Gregory Smith

Grant Program: Research and Development

Project Narrative

Rapid Pollution Off-Gassing Assessments of Museum Construction Materials by Gas Chromatographic Techniques
A Tier I NEH Research and Development Proposal

I. SIGNIFICANCE
Many pieces of our material culture spend a large portion of their existence in protective packages, for example display cases, vitrines, shipping crates, and storage containers. The relatively low air exchange rates of these enclosures require that the materials from which they are constructed do not off-gas corrosive or reactive chemicals that could harm the artwork within [1, 2]. Emissions from construction materials can arise from residual solvents, fire retardants, reactants, additives, plasticizers, as well as from degradation reactions of the materials that occur at ambient conditions or due to light exposure.

Larger museums dedicate considerable effort to screening potential construction materials using microchemical or accelerated corrosion tests [1, 2]. The preservation quality of enclosures and exhibition spaces relies heavily on the dedication of museum staff to a rigorous testing protocol and the accuracy of the tests used in their assessments. A critical issue in evaluating materials for use in museums is the incredibly wide range of potential pollutants and their normally low concentration levels. Additionally, the proliferation of new construction materials based on engineered composites, new plastics, and renewable biomaterials increases the need to rapidly screen these components for possible noxious emissions before adopting them for museum use. Given the current trend in relaxing previously stringent museum climate setpoints of relative humidity and temperature in order to save energy and reduce carbon footprints, it is expected that museums will need even more microclimate enclosures in the future to protect our most sensitive cultural objects [3].

Among the microchemical tests currently used to assess materials, specific color reactions have been developed for several detrimental chemicals commonly released by building materials. These contaminants include organic acids that react with pigments and metals or catalyze degradation reactions (the iodide/iodate test [4]), reducible sulfides capable of tarnishing metals (the sodium azide test [5]), chloride-containing materials that liberate hydrochloric acid (the Beilstein test [1]), and formaldehyde, a carcinogen that can lead to the creation of harmful formic acid (the chromotropic acid test [4]). These tests, however, do not detect the wider range of pollutants that can be generated by construction materials. These unobserved chemicals include unreacted monomers, solvents, volatile plasticizers, fire retardants, etc [1, 2]. Although the specificity of the microchemical tests can be a drawback, their advantage is the speed with which the assessment can be undertaken, usually within an hour, allowing for rapid feedback to exhibition designers, collection managers, and conservators awaiting test results. Rapidity of testing ensures safe alternative materials can be found even when museum staff must adhere to strict timelines for installing exhibits.

Perhaps the most common and widely accepted test method for assessing construction materials in museums, however, is the so-called "Oddy Test," an accelerated corrosion test named after Andrew Oddy, who first described the test in the 1970s [6]. The Oddy Test utilizes three polished metal coupons (lead, silver, and copper) as indicators of material off-gassing based on their corrosion when confined in a high humidity reactor with the materials under test. The sample is aged in a 60°C oven for 28 days, after which the coupons are "graded" by visually assessing the level of corrosion on their surfaces. This test provides an inexpensive approach to assessing construction materials and generates visual evidence for the damaging nature of the volatiles present in the sample material as well as those generated by

incipient degradation in the accelerated aging experiment. However, the Oddy Test has numerous drawbacks, including its sensitivity only to pollutants that give rise to metal corrosion, its subjectivity in grading the level of corrosion on the metal surfaces, its vulnerability to unspecified corrosion due to water condensation on the coupons, its failure to identify the actual pollutants or their concentrations, and its general unreliability when the same material is retested or tested by other institutions [1, 7]. Although test results have proven somewhat more consistent when practitioners follow stringent experimental controls [8], the inconveniently long duration before results are known often leads to shortcuts and reduced aging times that consequently invalidate the results.

Attempts have been made to alter or supplant the Oddy Test to make it faster and to provide more reliable results. The British Museum and the Metropolitan Museum of Art have created abbreviated versions of the Oddy Test [9, 10] in which multiple coupons are exposed simultaneously in a single reactor. Other researchers have sought to speed up the test by replacing the commonly used silver metal foil with a nanoparticulate or vapor deposited silver film that reacts more rapidly to pollution [11-13]. Reedy et al. adapted electrochemical tests from the electronics manufacturing industry as an entirely different approach to detect pollutants capable of corroding metals [7]. Although potentially quantitative, more reproducible, and rapid, these tests still are limited in the scope of their screening only to pollutants that lead to corrosion of metals, can take several days to complete, and fail to determine the exact identity or quantity of the corrosive pollutants. Researchers concerned largely with organic objects have developed a 5-day chamber test that uses a purified paper coupon as the detector. Damage to the cellulose due to pollutant exposure is monitored by dissolving the paper and measuring the viscosity of the resulting solution [14], a complicated and still time-consuming analysis.

Given the excessive duration, narrowly targeted compounds, and lack of reliability of current methods for assessing materials for harmful off-gassing, a dedicated research program to develop and optimize a rapid, objective, and quantifiable instrumental method of identifying volatile organic compounds (VOCs) is sorely needed in the museum field. The project team proposes to develop such an approach based on a rapid GCMS analysis to support or perhaps eventually supplant traditional approaches to materials suitability testing. The research expands and extends a current collaboration between the Indianapolis Museum of Art (IMA) Conservation Science Laboratory and a Butler University analytical chemistry professor toward developing an approach for VOC analysis using the sampling technique of evolved gas analysis (EGA) with cryo-trapping. Initial results have demonstrated its speed, reliability, sensitivity, quantitative nature, and ability to detect the broadest range of potential pollutants.

Ensuring the safety of construction materials used in proximity to artwork is one of the most important cultural heritage research topics because it affects every object in a museum's collection for the whole of its existence within the institution. Physical objects of cultural significance are the primary resource materials for all of the Humanities, and preserving them in as near to their original state as possible is a priority and responsibility of collecting institutions. **The IMA proposes to develop and optimize a gas chromatography-mass spectrometry (GC-MS) analysis protocol with a broadly applicable volatiles sampling strategy to provide rapid, quantitative, and molecularly specific assessments of the emissions from construction materials considered for use in museums. The instrumental protocol and resulting data will be made available to institutions around the globe and will directly impact confidence in the materials used within museums, libraries, and archives.**

The goals of the project are to further develop and optimize this approach using a sample test set of museum materials, including comparing it to other VOC sampling techniques being pursued in the field. Importantly, EGA in particular has not been considered as a possible alternative to materials suitability

testing. As such, a direct comprehensive comparison has not yet been performed in the museum field and will inform museum scientists as to the selection of the fastest and most reliable method for accurately assessing museum construction materials. Outside of conservation science, several smaller comparisons have been made on a very narrow group of analytes in fields such as industrial hygiene [15], food chemistry [16], and environmental chemistry [17]. Furthermore, although initial tests suggest the EGA technique can detect a wide range of volatile emissions, little is known about the visual and physical impact of these VOCs on museum materials. To investigate this, construction materials and individual pollutants observed in their emissions will be tested for their potential to damage museum collections using standard testing routines such as the Oddy Test and a modified version using a paper dosimeter to simulate damage to artworks made of organic materials. In the event that damage is observed, the concentration of particular pollutants that is required to cause incipient degradation, known as a lowest adverse effect level (LOAEL) [2], will be determined by testing an individual pollutant at a range of concentrations at near ambient conditions.

The proposed research will not only develop a much needed instrumental analysis protocol for museum scientists and allied fields, but will also foster a collaboration between neighboring institutions - Butler University is within 200 yards of the IMA campus - that will impact undergraduate education in chemistry. Funding is requested to contract the expertise of a faculty member of Butler University's chemistry department, as well as to support an undergraduate researcher to assist in the experimental work over the next two years. The research experience, training, and mentoring within this project will expose these scientists to the rich interface shared by the Arts and the Sciences.

II. BACKGROUND OF APPLICANT

Incorporated in 1883, the IMA is among the ten largest encyclopedic museums in the nation. Settled on 152 acres, the campus includes the Museum, the Oldfields-Lilly House & Gardens, The Virginia B. Fairbanks Art & Nature Park: 100 Acres, and an on-site conservation science laboratory. The IMA was one of ten museums to receive the National Medal for Museum and Library Service in 2009 for its demonstrated commitment to public service through innovative programs and community partnerships. In May 2015, the IMA launched a new ten-year strategic plan that provides a long-term vision and comprehensive plan for its future. This project would directly fulfill the goal to: **"Maintain best practices in collections management and conservation to preserve the collection, horticulture and environmental resources, and historic structures to the best of our ability."**

The 3000 square foot Conservation Science Laboratory at the IMA, shown in Figure 1, was constructed in March 2011 with support from Lilly Endowment Inc. Outfitted with state-of-the-art instrumentation in chromatography, spectroscopy, thermal analysis, light and electron microscopy, and accelerated aging and weathering chambers, the facility was planned with postdoctoral scholars, visiting fellows, and graduate student researchers in mind.

Figure 1. *Panorama view of the 3000 square foot IMA Conservation Science Laboratory. Additional instrumentation and accelerated aging chambers are located in adjacent laboratories.*

The proposed research will take place at the IMA. Key pieces of instrumentation are already available in the IMA Conservation Science Laboratory, including a dual injector GC (Thermo Trace Ultra) with a liquid, HS, and SPME robotic rail autosampler (Thermo Triplus), vial incubator, SPME fiber conditioning station, and pyrolysis sample introduction unit with EGA and cryo-trapping accessory (Frontier DoubleShot Pyrolyzer). The instrument is shown in Figure 2. The GC is coupled to both a single quadrupole MS detector (Thermo ISQ) and a thermoconductivity detector (TCD). The lab also operates a Thermo Accela ultra-high pressure liquid chromatograph (UHPLC) with autosampler and diode array detector (DAD) coupled to an LTQ quadrupole ion trap electrospray ionization mass spectrometer (ESI-MS). The UHPLC-DAD-ESI-MS instrument is covered under a manufacturer's service contract for the duration of the grant period. The laboratory is outfitted with bench space and chemical hoods suitable for sample preparation as well as ancillary equipment that will support the main project goals. Major instrumentation includes light and electron microscopes, x-ray fluorescence spectrometers, a modulated differential scanning calorimeter, handheld and fiber optic colorimeters, UV-visible spectrometer, a Raman microscope, and an FTIR microspectrometer.

Figure 2. *Thermo Trace GC Ultra with ISQ single quadrupole MS being operated by Butler University undergraduate summer research fellow Jericha Mill.*

Funding is requested to: renew the service contract on the GC-MS instrument for two years to ensure its availability for the project; obtain a SPEX cryogenic sample mill to prepare construction materials with a high, uniform surface area; and obtain some lab hardware to further augment these instruments.

Library holdings of the IMA and Butler University, as well as those available through Dr. Smith's adjunct appointment at Indiana University Purdue University Indianapolis (IUPUI), will be available to all project participants, providing superb literature resources in art history, conservation, materials science, and chemistry.

The IMA Lab, the Museum's award-winning software team, has a long history of collaboration and experience in developing tools and solutions that address important problems in museums. Members of the IMA Lab will provide support for the creation of online content generated during the grant period.

III. HISTORY, SCOPE, AND DURATION

In the fall of 2014, Dr. Michael Samide, Professor of Chemistry at Butler University, participated in *Project MUSE: MUseum Sabbatical Experiences for Faculty Teaching at the Arts-Science Interface*, a Dreyfus Foundation funded program at the IMA. *Project MUSE* gives college and university chemistry professors an opportunity to spend 3-6 months in the Museum's laboratory conducting technical studies of the collection or arts-based scientific research in order to augment their chemistry curriculum at their home institution. Dr. Gregory Dale Smith, Otto N. Frenzel III Senior Conservation Scientist at the IMA, and Dr. Samide worked together to lay the foundation for the present grant, exploring new instrumental methods for the analysis of VOCs emitted by museum construction materials. This collaboration continued into the first half of 2015 with Dr. Samide spending one day per week at the IMA continuing to develop, optimize, and test the EGA sampling strategy on museum materials. In summer 2015, Dr. Samide and Butler undergraduate student Jericha Mill were awarded a grant from the Butler Summer Institute to continue working on the project at the IMA. This collaboration has yielded a manuscript that has been submitted for publication to a peer-reviewed scientific journal [18] and that will also form the core of an invited presentation by Dr. Smith at the upcoming conference "Conservation and Exhibition Planning: Material Testing for Design, Display, and Packing" to be held in November 2015 at the Smithsonian American Art Museum.

At this stage, the project team has developed a working method for testing a potential construction material's off-gassing potential in order to yield a quick assessment of its suitability for museum use. The present EGA-GC-MS protocol can generate a comprehensive VOC profile of a material in approximately 25 minutes, presenting a significant time advantage over the currently used month-long Oddy Test. Simple test methods such as the Oddy Test are incapable of identifying specific pollutants or determining their concentrations. The project team has shown the potential for semi-quantitative and quantitative analysis of specified pollutants depending on the availability of appropriate surrogate analytes and reference standards, respectively. Although other cultural heritage researchers have used chromatographic techniques to assess museum construction materials [19], EGA has not been used for this in the past, and to our knowledge only a single research effort exists on the use of this technique in cultural heritage to identify plastics [20]. Furthermore, attempts at quantification of VOCs in testing museum materials suitability have generally dealt with measuring pollutants in existing casework [21-23] and not in the initial assessment of museum materials.

Figure 3 shows the EGA-GC-MS chromatogram of VOCs generated from the analysis of black polyurethane packing foam. A similar material was studied by the Metropolitan Museum of Art using SPME [24] after degradation products were found on an object stored for 10 years in the foam. Their analysis used different SPME adsorption fibers and many hours of lab time to generate essentially the same pollution profile as the single EGA experiment shown here. Moreover, the IMA research team has been able to quantify the 4-alkylmorpholine pollutants through the use of a surrogate analyte, 4-ethylmorpholine, as shown in the associated table. Morpholine compounds of the generic structure

shown in the figure are used as catalysts in the production of the foam. The results in this instance are only semi-quantitative with errors ranging from 14% to 32% due to the use of a single surrogate analyte versus a pure reference standard for each pollutant and also due to the heterogeneous nature of the foam material. In a similar analysis of acetic acid emitted from common poly(vinyl acetate) (PVAc) glues (not shown here), analytical quantification was possible due to the use of a high purity acetic acid reference standard, and the associated errors were between 0.13 and 9%.
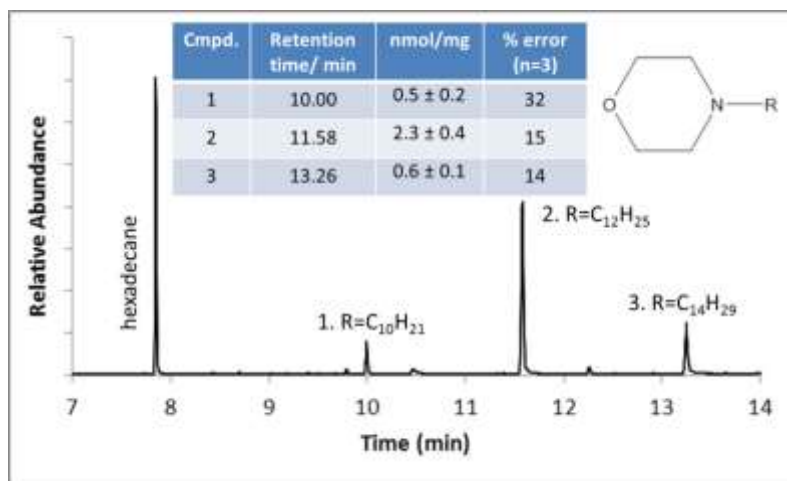

Figure 3. Chromatogram for the EGA-GC-MS analysis of polyester-based polyurethane foam. Alkylmorpholines were detected as 4-decylmorpholine (10.00 min), 4-dodecylmorpholine (11.58 min), and 4-tetradecylmorpholine (13.26 min). The large peak at 7.85 min is the internal standard (hexadecane) used for quantitation. Other pollutants identified included higher and lower morpholine analogs, a hindered phenol antioxidant, and a cyclic diester formed as a reaction byproduct of polyurethane synthesis.

The EGA-GC-MS technique holds promise for developing a protocol to assess the widest range of volatile and semi-volatile pollutants from museum construction materials while delivering quantitative data in a rapid turnaround time of less than 30 minutes. Further work is necessary to optimize and develop the methodology, to better understand the usefulness and limitations of the quantitation of these chemicals, and to understand the minimum concentrations of various VOCs that are necessary to actually cause damage to cultural heritage objects with a wide range of compositions (metal, glass, plastic, paper, leather, etc.). During the proposed two year project, researchers will compare the EGA technique developed at the IMA to other instrumental techniques practiced in the field, to understand the reliance of off-gassing on the accelerated conditions used in the experimentation and on the size and shape of the samples introduced in the testing, as well as to develop a reliable testing methodology to be practiced at other museums around the world. Beyond the grant period, the instrumentation and protocols developed will be used in fundamental studies of organic pollution concentrations and their impact on museum collections (a continuation of Phase 3 below), as well as understanding the potential role of museum objects themselves to serve as a source of pollution in museum enclosures. This line of study is anticipated to be a key component of the IMA/Butler University collaboration for many years and to be the subject of further grant proposals.

IV. METHODOLOGY AND STANDARDS
Research is comprised of three sequential, but overlapping phases. During Phase 1, researchers will select a representative group of construction materials to form a test sample set to be studied in depth

during the research program. Although proof-of-concept data has already been established for the viability of the EGA technique, various aspects of sample pre-treatment will be studied to determine the optimum approach to EGA-GC-MS, and this sampling approach will be compared to other chromatographic sampling approaches currently being investigated at museums around the world [19]. With the anticipation that many advantages in VOC analysis will lie solely in the EGA technique proposed here, Phase 2 will examine whether the presence of a potential pollutant identified by EGA-GC-MS actually leads to degradation reactions in museum collection materials. To do this, accelerated degradation tests such as the Oddy Test and another modified accelerated degradation test using an organic surrogate, viz. purified Whatman filter paper, will be undertaken using the test materials from the sample set as well as pure reference chemicals for the potential pollutants. Phase 3 will explore the role of quantitation of pollutants through EGA-GC-MS with the goal of establishing the "lowest adverse effect levels" (LOAEL) [2] for specific pollutants identified in Phase 2 of the project.

Phase 1: Sample Selection and Technique Comparison

Phase 1 will begin with the selection of a representative list of materials to form a test sample set for the entire project duration. In collaboration with the IMA's collection care division, researchers will create a corpus of 24 sample materials. These materials will be selected based on their pertinence to museum storage and display, utilizing the institution's long history of materials testing. The sample set will include materials that have previously passed the Oddy Test and are regularly used within the institution, those that have repeatedly failed the test, and others that have given inconclusive results. A representative list of examples with justifications is provided in Table 1. In some instances, multiple versions of the same material obtained from multiple manufacturers or different production batches will be included to highlight the variability that exists in manufacturing processes.

Material	Justification
Polyurethane packing foam (ester and ether varieties)	This material has been studied by several labs and, although often used for short term applications, it has been found to cause white crystalline deposits on artwork stored for longer periods.
Expanded PVC board	This material is finding many uses in museums because it is inexpensive, easily machined, and rigid. Oddy Test results at IMA from different manufacturers (Sintra, Excel FF, Celtec) have given conflicting results.
Polyethylene foam	Many museums use Volara brand PE foams, but other versions have failed when used for long term storage.

Table 1. *An example of materials to be included in the sample test set with rationale for their selection.*

Off-gassing from the material under test and equilibration with the surrounding environment can be enhanced by grinding, gentle heating, and agitation of the sample container prior to sampling. All of these factors can be controlled and automated by instrumentation. The sample volume and form, heating duration, and incubation temperature will be optimized to strike a balance between liberating the most volatiles from the sample, including incipient degradation products, while maximizing speed and avoiding excessive moisture and temperatures that are capable of engendering non-ambient degradation pathways, a common criticism of the Oddy Test [7]. To study the effect of sample surface area on VOC emissions, materials forming the sample set will be studied in two forms: the "as-used" form, such as thin coating, sheet, or large block; and also as a fine, uniform particulate generated using a cryogenic mill. The mill specified in the project budget utilizes liquid nitrogen (-196ºC) to embrittle samples prior to impact grinding to generate a micrometer sized particulate powder with very high surface area. The cryogenic milling eliminates sample heating that might drive off volatiles while also

facilitating the grinding of soft materials like plastics, elastomers, or foams. Both the low and high surface area samples will be studied by the EGA technique to identify the pollutants released in each instance and their concentrations.

Phase 1 will also compare the EGA technique to other VOC analysis techniques that are currently being pursued in other museum laboratories [19]. These approaches include SPME, static HS analysis, TD analysis, and EGA. Figure 4 shows the differences in these approaches schematically.
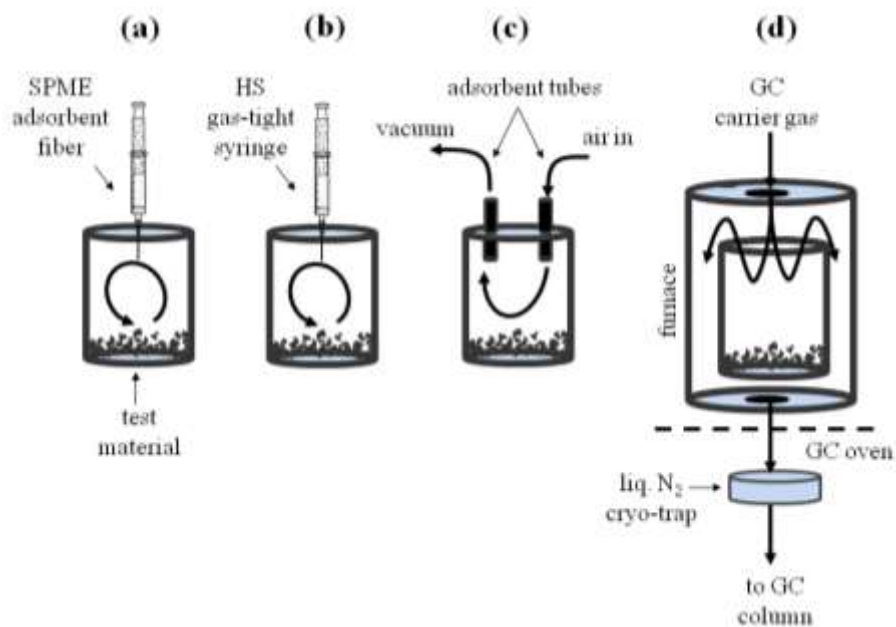

Figure 4. *Sampling strategy schematics comparing (a) solid-phase microextraction, (b) static headspace, (c) thermal desorption, and (d) evolved gas analysis with liquid nitrogen cryo-trapping.*

•**SPME:** Solid phase microextraction for GC-MS uses a solid stationary phase adsorbent coating on a flexible syringe fiber to pre-concentrate the analyte on the sample device prior to insertion and desorption in the hot GC inlet. A schematic representation of the SPME sampling protocol is shown in Figure 4(a). The fiber is introduced into the sample container or sampling environment for a specific period of time, minutes to hours, to absorb the analytes based on their affinity for the fiber material. Heating and agitation of the sample container prior to or during sampling speeds the equilibration of volatiles within the sampling environment.

A significant advantage of SPME is the ability to pre-concentrate the analytes on the SPME adsorbent and thereby increase the sensitivity of the technique. The success of the pre-concentration step depends largely on the selection of the adsorbent phase and exposure time, and numerous fibers with varying adsorbent chemistries can be purchased or made in the laboratory. Pre-concentration steps can last several minutes to several days. The chemical nature, thickness, and porosity of the coating all directly influence the specificity and sensitivity of the fiber to the adsorbed analytes. In this work, each material in the sample test set will be examined using short pre-concentration steps on a total of three commercially available fibers ranging in polarity of the adsorbent phase. As stated previously, in the analysis of polyurethane packing foam at the Met, three such fibers were required to get a representative analysis of the VOCs emitted [24]. It is anticipated that some of the more polar or highly volatile target analytes will require derivatization for efficient collection on the SPME fiber and

separation in the GC column. Derivatization can be achieved by pre-treating or post-treating the SPME fiber in an appropriate derivatizing agent. As examples, reagents such as 1-phenyldiazomethane (PDAM) and o-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA) have served to enhance the collection and separation of degradation byproducts sampled by SPME [24]. The potential need for derivatization combined with the sometimes lengthy pre-concentration step can slow down and complicate the SPME approach to VOC analysis.

A handful of conservation papers describe SPME analyses in the cultural heritage sector. Experiments have been conducted targeting degradation products from aging books [25-27], plasticizers in document encapsulating plastics [28], acetic acid in the museum environment [29], off-gassing from wax sculptures [30], degradation products from iron gall inks [31], and even limited testing of the atmospheres inside Oddy Test jars [12, 14, 24, 32]. The applications in forensic science [33, 34], environmental chemistry [35], and industrial hygiene [36, 37] are much more numerous.

•**HS:** Static headspace sampling withdraws the atmosphere directly surrounding the contained test material without pre-concentration for analysis by GC-MS. In static HS, shown schematically in Figure 4(b), the equilibrated headspace gases are collected by a gastight syringe and injected directly into the GC inlet. Because the technique captures all of the volatiles in the headspace and does not rely on a target molecule's affinity for a particular adsorbent, it can be a less specific and therefore a more general sampling strategy, a distinct advantage when testing construction materials where the chemical nature of the pollutants is not known in advance. Several recent publications have compared the performance of static HS sampling with SPME for GC-MS analysis with varied results [38-40]. The performance of each technique is sample dependent, with some reports favoring SPME [38, 39] while others showed better performance by HS [40, 41]. Static HS analysis suffers from lower intrinsic sensitivity, requiring pollutants to be present at concentrations that are detectable without pre-concentration.

Static HS sampling for GCMS has seen only a few uses in the field of cultural heritage chemistry, including the analysis of degradation products from iron gall ink documents [42] and quantification of residual ethylene oxide in disinfected paper documents [43] and photographic papers [44]. This sampling approach has not been applied to museum material suitability testing to our knowledge, but will be compared here for the first time.

•**TD:** The thermal desorption technique circulates a flow of purified gas over the contained sample and out through a tube filled with adsorbent material such as activated charcoal or Tenax TA (2,6-diphenylene oxide). Figure 4(c) compares the TD sampling strategy to the other proposed approaches. Volatiles contained in the HS are collected onto the desorption tube's stationary phase as the gas is pulled through the container. Because of the dynamic flow, the gas-liquid equilibrium of the analytes is continually disturbed, causing more volatilization as the target molecules in the headspace are pre-concentrated onto the adsorbent tube. Sample heating and agitation can further increase the rate of off-gassing and improve the sensitivity of the technique over static HS analysis. After pre-concentration, the adsorbent tube is heated in a special apparatus connected to the GC inlet in order to release the collected pollutants into the chromatograph for separation and identification. Museum casework and construction materials have been previously analyzed by TD [21-23], but like SPME, the sampling strategy requires lengthy pre-collection steps and also requires that the analytes share an affinity for the adsorbent phase in order to be detected. Despite this, TD has been adopted as a standard testing procedure in the buildings trade to detect construction materials that generate irritating pollutants responsible for "sick building syndrome" [45]. Due to the specialized equipment necessary for TD, it will

not be directly compared in this study. However, construction materials that have been previously analyzed by TD will be included in this study's test set so that a comparison can be made to results already present in the literature.

•**EGA:** Evolved gas analysis uses a heated sample furnace to directly introduce emitted pollutants from a sample into the GC carrier gas stream as shown in Figure 4(d). In the version of this technique practiced at the IMA, the sample holder is lowered into an isothermal (115℃) furnace so that the pollutants emitted from a small test sample are collected, focused, and concentrated onto the head of a cool capillary GC column. If necessary, a liquid nitrogen cryo-trap accessory applied to the column head can be used to freeze out and collect very volatile pollutants. Once the optimum temperature and heating duration have been applied, the cryo-trap is disengaged and the GC temperature ramp begins, re-volatilizing and separating the condensed pollutants prior to detection by the MS. The EGA approach combines many of the advantages of the static HS, SPME, and TD analyses. Like HS analysis, EGA sampling is non-exclusive; there is no intermediate adsorption step, so all VOCs emitted by the material are analyzed by the GC-MS. Like TD analysis, the sample is exposed to a flowing gas, generating a non-equilibrium state that encourages additional emission of volatiles in the hot furnace. Like TD and SPME, sample pre-concentration can be achieved by longer heating and cryo-trapping stages prior to engaging the GC analysis. Good results have been obtained with only a 30 second heating followed by a 25 minute analysis run by GC-MS. So far the project team has studied over 25 different construction materials by EGA.

Phase 2: Determination of the Damage Potential of VOCs
It is anticipated that following the comparison in Phase 1, EGA will remain a competitive assessment strategy with several advantages over the currently practiced Oddy Test and the more recent chromatographic approaches discussed above. In the EGA studies completed so far at the IMA, numerous VOCs were identified as emanating from museum construction materials. In several instances, the materials under test – for instance Plexiglas sheet – were commonly regarded as being benign in the museum environment and are already widely employed for storage, transport, and display of museum objects. Based on this practical experience, one can assume that the volatiles emitted by the construction product (primarily methacrylic acid in Plexiglas) are incapable of doing damage to the wide range of materials from which artwork is created, at least at the concentrations commonly encountered in the museum. However, construction materials that repeatedly or even occasionally failed the Oddy Test also generated a host of gaseous pollutants. But which of these chemicals is actually responsible for the aggressive attack? And at what level must the pollutant exist in order to cause damage to metals, paper, leather, or plastics?

Phase 2 will address these questions by comparing the VOC profiles of the test set materials to the performance of those materials in traditional Oddy Testing and in a similar test using a paper dosimeter. In this way, volatile emissions can be assessed for their potential negative impact on artworks of both organic and inorganic compositions. Oddy Tests will be performed every other month for a period of one year on all 24 of the materials in the test set, generating a large group of replicate analyses. These assessments will be performed on the material in its "as-used" state, as well as on the comminuted powdered samples.

In addition, paper dosimeters aged along with the test materials will be assessed for degradation caused by the same VOCs. Purified paper is prone to primarily hydrolysis and oxidation reactions when exposed to pollutants. These reactions lead to chain scission in the paper, discoloration, and loss of mechanical strength. Although the decrease in molecular weight for the paper has been assessed by fold endurance

testing [46] and also by direct measurement of the degree of polymerization of the cellulose [14], another indication of the degradation is the formation of monomer and oligomer saccharides. These can be solvent extracted, identified, and quantified. An unpublished testing protocol developed by Dr. Eric Breitung at the Library of Congress uses ion chromatography to quantify these degradation products in a paper dosimeter version of the Oddy Test [47]. IMA research plans to develop a modified mass spectrometry approach demonstrated by Stephens et al. [48] in conjunction with liquid chromatography to separate, identify, and quantify these carbohydrate degradation products. This represents a new approach to paper dosimetry in the field of conservation science. Increases in the mono-, di- and oligosaccharide concentrations of the extracts will indicate VOC emissions capable of damaging cellulosic materials. Through this combination of accelerated degradation tests will be generated comparative data for the deleterious effects of certain museum construction materials on both inorganic and organic surrogates representing a wide array of cultural heritage objects.

Phase 3: Quantitation and LOAELs

The EGA technique has already shown promise as a quantifiable assessment of pollutants emitted by potential museum construction materials. Quantification has rarely been attempted in the vetting of these materials in the past, and questions remain as to what exactly is being "quantified" during accelerated testing protocols. For example, the EGA technique is run at an exaggerated temperature, and because it is a microanalytical approach, it utilizes small samples with an abnormally high surface area compared to the mass of material. These experimental features enhance the sensitivity of the technique to measure low level emissions from the material, but they also present an "unnatural" situation in terms of the pollution environment generated in the accelerated laboratory test. Quantification of the emitted pollutants under these conditions can be of direct benefit, for instance selecting between two similar materials analyzed under identical conditions: the one with the lower pollution levels should be chosen if all other considerations are equal. Furthermore, some pollutants such as formaldehyde are so aggressive that merely discovering their presence may lead conservators to avoid a material altogether. But how will a material with a pollution profile that contains low levels of a noxious gas behave under normal conditions of use? Should it be discarded outright, keeping in mind that "the dose makes the poison?"

Phase 3 will explore the relationship between the exaggerated pollution measurements represented by the EGA and Oddy Testing techniques with the levels of pollutant generated under "as-used" conditions. In addition, the project team will determine the minimum concentration of a few select VOC pollutants required for actual degradation to occur in a normal museum environment. These data are available for a very small number of pollutants of worldwide concern, for instance NO_2 and ozone [2], but almost no data exist regarding most of the VOCs encountered in museum construction materials.

The amount of a specific VOC emitted from a material is a function of the mass of material, its surface area, and temperature. In this study, the quantity of a VOC emitted from a material during EGA will be reported in units of mass of VOC per mass of sample (e.g., ng VOC/mg material) for materials of known surface area. Because the EGA technique operates using elevated temperatures to accelerate the emission of VOCs, some relation back to ambient temperatures is necessary to understand the emissions expected under display conditions. To determine this relationship, quantitation will be performed on a few model materials at a series of temperatures ranging from 115ºC to 60ºC, and a plot of quantity versus temperature will be generated and extrapolated to room temperature. The experimentally extrapolated room temperature emission can then be compared to experimentally determined LOAELs as described below.

The project proposes to measure the LOAEL for a few selected pollutants determined in Phase 1 and 2 for the test sample set and to establish a methodology to extend this data set in the future. Traditionally LOAEL data has been generated by measuring weight gain in metal coupons exposed to increasing concentrations of a reference pollutant compound over several months or years [2]. The project will use this approach to determine the LOAEL of a specific pollutant, e.g. organotin thiols, and compare that to the off-gassing behavior measured for materials that are a source of this pollution. Organotin thiols are widely used as heat stabilizers in PVC sheet plastics and have been implicated at the IMA in the tarnishing of silver objects stored in display cases constructed of Sintra PVC boards. The same compound may also be damaging when used to store and display artworks of an organic nature. The same pure chemical can be tested using the paper dosimeter approach above to gauge the LOAEL for a cellulose surrogate for organic artworks. Other VOCs found to cause damage in the Phase 2 testing of materials using traditional metal coupon Oddy Testing and paper dosimetry will be explored as time allows.

This approach to determining LOAEL, however, is not effective in all instances, for example when a pollutant does not corrode metal surfaces or lead to hydrolysis of cellulose. Many of the VOCs encountered so far though EGA experiments at the IMA are not expected to be problematic with these materials, but could potentially lead to other chemical reactions in artists' materials like forming offensive surface deposits, discoloring artwork, and softening plastics. Although this research effort will not fully resolve the question of "how much is too much" for all pollutants, it endeavors to add to the growing understanding of the "damage function" of museum pollution using two classes of surrogates.

The successful completion of Phases 1-3 of the proposed research will benefit collections care staff at museums around the world as they tackle one of the more vexing issues in preventive conservation – the timely selection of construction materials that will protect artwork during storage, display, and transportation. This project will develop a rapid, comprehensive chromatographic technique for the comparison and selection of museum construction materials, offer a better understanding of which specific gaseous emissions should be rightly termed "museum pollutants" based on their demonstrated ability to damage artworks, and provide a greater understanding of the concentration of certain common VOCs that lead to damage in artwork.

V. WORKPLAN

The proposed project will span two years, and is comprised of three sequential, but overlapping phases as detailed in the previous section:

Phase 1: Sample Selecting and Technique Comparison *(January 2016 through December 2016)*:
Activities will include: select and purchase sample set (Jan 2016); intern recruitment (Jan-Feb 2016); purchase of cryogenic sample mill (Jan 2016); online teaching module for VOC analysis goes live (Jan 2016; updates to continue throughout grant period); comparison of "as-used" versus ground samples for EGA of sample set (Jan-Aug 2016); comparison of VOC sampling techniques on sample set (May-Aug 2016); preparation and submission of manuscript for Phase 1 (Oct-Dec 2016).
Phase 2: Determination of Damage Potential of VOCs *(January 2016 through December 2017)*:
Activities will include: initial development and testing of LC-ESI-MS analysis of paper dosimeters (Jan-May 2016); Oddy Testing of sample set materials (Apr 2016–Apr 2017); paper dosimeter testing of sample set materials (May 2016-May 2017); upload of testing results to AIC Materials Database wiki (May 2016-May 2017); preparation and submission of manuscript for Phase 2 (May-Dec 2017).
Phase 3: Quantitation of LOAELs *(April 2016 through December 2017)*:
Activities will include: determine LOAEL for organotin thiols on metals (April 2016-Dec 2017); determination of LOAEL for organotin thiols on paper (May 2016-Dec 2017); measurement of

concentrations versus temperature and extrapolate to room temperature (May-Aug 2017); preparation and submission of manuscript for Phase 3 (Dec 2017-Post-grant). [Please see Appendix B: Project Workplan and Timeline]

VI. STAFF

Dr. Gregory Dale Smith, Otto N. Frenzel III Senior Conservation Scientist, will act as Project Director. He will oversee implementation of laboratory research, be responsible for reporting outcomes, and will supervise the undergraduate intern. Smith holds a Ph.D. in Analytical and Physical Chemistry from Duke University and has spent the past ten years teaching and researching in the area of traditional materials suitability testing for museums. As the Andrew W. Mellon Assistant Professor in Conservation Science in the graduate art conservation training program at SUNY Buffalo State College (2005-2010), Smith was responsible for creating the program's first course in preventive conservation, comprising over 18 lectures and 6 laboratory exercises on preventive conservation topics. One of the student laboratories resulted in new data on Oddy testing that was presented at the meeting of the International Council on Museums – Conservation Committee (ICOM-CC) in New Delhi, India in 2008 [49]. In his five years at Buffalo, Smith trained over 60 new conservators in the art and science of testing materials for potential negative impacts on artwork. He maintains an adjunct academic appointment in the Forensic and Investigative Sciences program at IUPUI, where he teaches a graduate chemistry course on the scientific analysis of fakes and forgeries. He has been the principal advisor for one Masters level graduate student who conducted a two year study of the evaporation behavior of cleaning solvents on painted surfaces using static headspace (HS) analysis with GC-MS; that student now occupies the position of forensic chemist at the Indiana State Department of Toxicology. He has mentored 26 students and scientists in his laboratory over the course of the IMA Conservation Laboratory's five year history. He will spend approximately 195 hours/year of his time on this project. [Please see Appendix D: Biographical Sketches of Project Staff]

David Miller, Senior Paintings Conservator and Chief Conservator, will participate as an advisor, grounding analyses in typical museum practices and good collection stewardship. Miller holds a Master's degree and Certificate of Advanced Study in Art Conservation and has over 30 years of materials suitability testing and environmental monitoring as a conservator at the IMA. He has developed microclimate cases for museum objects and paintings on loan from the IMA, and will bring invaluable experience to the practical side of materials selection and utilization. He will spend approximately 24 hours/year on this project. [Please see Appendix D: Biographical Sketches of Project Staff]

Laura Mosteller, Senior Conservation Technician, will prepare, run, and interpret Oddy Tests using metal and paper dosimeters. Mosteller has served as Senior Conservation Technician since 2004 at the IMA and her years of experience in administering Oddy Tests will be utilized in the traditional assessment techniques for vetting museum construction materials. She will spend approximately 90 hours/year on this project. [Please see Appendix D: Biographical Sketches of Project Staff]

Mike Bir, Director of Collection Support and Special Projects, will provide practical guidance in selecting and studying the sample testing set for the project based on his knowledge of museum casework fabrication, wood and metal shop fabrication techniques, and installation methods for artwork. Bir joined the IMA in 1990, with experience in the Museum's collection care division as a conservation mount maker, exhibit designer, and as the leader of the IMA's fabrication shops and art installation crews. He will spend approximately 32 hours during Year 1 and 24 hours during Year 2 on this project. [Please see Appendix D: Biographical Sketches of Project Staff]

Kyle Jaebker, Director IMA Lab, will provide technical assistance in establishing a GitHub site for dissemination of project data. Since 2009, Jaebker has used his background in software development to build technology solutions for a variety of Museum projects, including the development of the OSCI Toolkit, an open-source project to create a suite of tools to facilitate the publishing and broad dissemination of online scholarly catalogues for art history. He will spend approximately 10 hours/year on this project. [Please see Appendix D: Biographical Sketches of Project Staff]

<u>**Grant Contract Staff**</u>
Dr. Michael J. Samide, Professor of Chemistry at Butler University, will serve as Research & Development Faculty Fellow for the project and will assist the Project Director in implementation of laboratory research, as well as supervise the undergraduate intern. Samide has researched the analysis of volatiles in environmental and food chemistry for over half a decade at Butler University, including patenting a new solid-phase microextraction (SPME) device for sampling VOCs [50] and the creation of a simple EGA accessory for undergraduate laboratory teaching [51]. His teaching responsibilities include introductory courses for chemistry majors and non-majors as well as advanced chemistry courses in analytical chemistry, instrumental analysis, and undergraduate research. Dr. Samide holds a Ph.D. in Analytical Chemistry from Indiana University. He will spend 10 weeks each in summers 2016 and 2017 on this project. [Please see Appendix C: Letter of Commitment; Appendix D: Biographical Sketches of Project Staff; and Appendix E: Job Descriptions for Contract Staff]

Research & Development Undergraduate Chemistry Intern. The IMA intends to hire one Undergraduate Chemistry Intern from Butler University as part of this grant. Under the supervision of Drs. Samide and Smith, the intern will be involved in all aspects of the project, from generating data using the various instrumental techniques, to preparing and running microchemical and accelerated aging tests, to writing reports and analyzing data. The Intern will be recruited during the first year of the grant with hope of maintaining his or her involvement throughout the two year grant period. The intern will spend approximately 10 weeks each in summers 2016 and 2017 on this project, plus hours appropriate to course credit at Butler University during the academic semesters. [Please see Appendix E: Job Descriptions for Contract Staff]

VII. SUSTAINABILITY AND EVALUATION
As the largest visual arts institution in Indiana, the IMA is committed to maintaining, preserving, and providing long term access to its assets. Data generated in the course of the research will be saved in a variety of digital and physical formats, and all files will be subject to the IMA's existing Data Retention, Backup and Disaster Recovery procedures. Data created by the IMA's Conservation Science Lab will be stored on enterprise class Storage Area Network (SAN) hardware and will be mirrored to an offsite facility. Continual weekly snapshots and nightly differential backups are made to magnetic tape libraries, which are stored offsite for a period of 2.5 months. The IMA Conservation Science Lab provides adequate and secure cabinetry for indexed sample storage and reference materials.

The primary outcome of the project research is the development of a rapid, quantitative, and reliable GC-MS analysis protocol for determining the suitability of construction materials considered for use in the museum environment. Each phase of research is anticipated to warrant individual publications in peer-reviewed journals, and basic bibliometric measures such as paper/presentation count and citation count will help indicate impact of the research. Additional outcomes include advanced training for an undergraduate scientist, and a repository of well characterized materials suitable for use by smaller cultural heritage institutions that might not otherwise be able to conduct their own testing.

The project team is committed to ongoing research in the area of traditional materials suitability testing for museums. Post-grant research is anticipated to continue as this technique and associated chromatographic techniques are used to examine preservation issues related to the IMA's collection. This anticipated next phase of research could benefit from the study of varied collections materials from other institutions.

VIII. DISSEMINATION AND INTENDED AUDIENCE

While the analytical approaches explored in this research will be repeatable only at the world's largest museum laboratories with the requisite scientific staff and instrumentation, the results generated from these tests will have universal applicability to those charged with the protection of our cultural heritage. Additionally, research at the interface of the Arts and the Sciences is a compelling tool to interest a wider audience of students in chemistry, and conversely to expose more scientists to the importance of protecting our cultural heritage. Therefore, three distinct audiences exist for this research, and they must be reached through distinct means.

For the first group, representing museum and academic scientists involved in cultural heritage research, as well as industrial hygienists and mainstream chemists researching VOCs, dissemination will take the form of peer-reviewed publications in the scientific literature and lectures at national and international conferences. To this end, funding is requested to allow members of the project team to attend at least two conferences per project year. General meetings, such as The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy (Pitconn) or the American Chemical Society National Meeting, are possible venues, as are specialist meetings of museum scientists, such as the Mass Spectrometry and Chromatography Users Meeting (MaSC) or the Indoor Air Quality (IAQ) Meeting. Each distinct phase of the research will generate sufficient new and relevant data to warrant individual publications in targeted peer-reviewed journals. Access among scientists to research summaries, tables of results, and raw data will be possible through an IMA GitHub site dedicated to the project. The Museum's software development team, IMA Lab, is already a regular user of this service, and will assist in this aspect of dissemination.

The IMA Conservation Science Laboratory also maintains a focus on undergraduate and graduate education for physical scientists with an interest in the Arts. The previously mentioned *Project MUSE* has already brought five college chemistry faculty to the Museum for sabbatical or summer research stays. As part of that project, participants are working to develop a series of freely available, interactive, online teaching modules for students ranging from high school to graduate levels. The tool provides a platform for teaching chemistry at the interface of art, making use of photos, graphics, videos, data, and methodology developed at the IMA. Dr. Samide's module focuses on teaching VOC analysis through the lens of pollution-related research in museums. This will continue to be a vehicle for dissemination of project research. [Please see Appendix F: Sample Images from Online Teaching Module]

For the third group of stakeholders, consisting of conservators, collections managers, and museum preparators, the valuable data generated through the research project will be made available within the field, but it is important that these constituents also understand how the data is generated. To that end, presentations at conservation workshops and meetings will demonstrate the analysis protocol, the interpretation of the data, and the limits of this approach to material suitability testing. The performance of materials in replicate tests will also be posted to the American Institute for Conservation (AIC) Materials Database wiki page, a valuable free service enabling institutions around the world to share the results of their testing with colleagues (http://www.conservation-wiki.com/wiki/Oddy_Tests:_Materials_Databases).