2017

Quantitative Analysis of Acetic Acid in Hard Woods as a Way to Improve Museum Artifact Storage

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Thesis title: Quantitative Analysis of Acetic Acid in Hard Woods as a Way to Improve Museum Artifact Storage

Intended date of commencement: 5/12/17

Read, approved, and signed by:

Thesis adviser(s): [Signature] 4/21/17

Reader(s): [Signature] 4/21/17

Certified by: [Signature]

Director, Honors Program 4/21/17

Date
Quantitative Analysis of Acetic Acid in Hard Woods as a Way to Improve Museum Artifact Storage

A Thesis
Presented to the Department of Chemistry
College of Liberal Arts and Sciences
and
The Honors Program
of
Butler University

In Partial Fulfillment
of the Requirements for Graduation Honors

Alexandria Spencer Flora
May 6, 2017
Acknowledgments

I would like to extend my gratitude to my advisor Dr. Samide for his guidance and the opportunity to work on this project. I would also like to thank Dr. Lantzer and the rest of the Honors Department for their support throughout my undergraduate career.
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Abstract

Many materials used for storage of museum artifacts have been found to cause damage to the items either through emitting harmful volatile gases or through direct contact. Harmful storage techniques can cause corrosion, discoloration, or deterioration of priceless artifacts. Museum enclosures made of hardwoods have been shown to emit acetic acid vapors that cause damage to the items being stored. In the present study, a review of the effects of acetic acid damage on museum artifacts was performed, and an evolved gas analysis and titration method were used to quantify acetic acid in various hardwoods.
Introduction

Museum Artifact Storage

Items of cultural and historical significance stored in museums are priceless; unfortunately, the conditions in which items are stored can possibly cause corrosion or deterioration. It is important to prevent historical and irreplaceable artwork and artifacts from being damaged in museum environments due to storage conditions. Museums utilize numerous conservation techniques in order to preserve collections.

The use of proper handling, displaying, and storing of historical artifacts is vital for preserving collections for future generations. Museum collections fall into two categories: inorganic and organic. Inorganic collections are those from nonliving materials such as stone, ceramics, and metals. Organic collections are those from animal products such as fur, wool, ivory, etc. In general, inorganic artifacts are more stable and, therefore, less susceptible to damage than organic artifacts. Paintings in art museums undergo changes due to both natural aging and damage. Aging can cause pigments to become more transparent and varnish to darken; however, some artists desire the aging of varnish and color in their paintings. Textiles such as tapestries, embroidery, and oriental carpets, some dating back to medieval periods, need to be handled with care and the knowledge of how storage of these can cause chemical and physical damage to the artifact. Methods of restoration of textiles are chosen based on the physical structure of the material, and it is useful to utilize microscopy in determining composition.

For the conservation of paintings, the original support on the canvas can be consolidated by attaching reinforcing fabric to the back of the painting using an adhesive. A common type of adhesive used for this process is a pressure-sensitive adhesive, which are typically synthetic
One study looking at these synthetic adhesives showed that thermo-oxidative aging causes three types of alterations: dehydration, oxidation, and cross-linking, which resulted in a significant loss of adhesive properties. Paper objects such as books, maps, drawings, and letters will suffer from discoloration and deterioration when mounted on an acidic material.

Handling of artifacts by humans should be kept to a minimum due to the oils, salts, and acids from human skin that have been known to damage many types of materials over time. When assembling a display or moving an object, it is vital for hands to be washed, lotion free, and to wear cotton or latex gloves. Moving one artifact at a time is ideal, and work space should remain clear to avoid contamination. The environment in which an artifact is stored is important for long-term preservation; moreover, numerous environmental factors can play roles in damage of artifacts. Environmental factors such as light, humidity, temperature, air pollution, and pests are all important considerations when storing an artifact in a museum. Museums should control for these factors throughout storage and exhibition of the items.

Ultraviolet light, infrared light, and visible light can all cause harm to artifacts, and UV light is considered the most harmful to objects. Light damage is both cumulative and irreversible. Light damage affects textiles, paints, and paper by weakening, fading, and darkening objects due to exposure. Temperature and humidity are also contributing factors to artifact damage that need to be controlled for. Temperature of storage should be tailored to the type of object being stored; however, many museums store mixed collections. A stable temperature for mixed collections is 68 to 72 degrees Fahrenheit with humidity levels of approximately 45–55%. Gaseous and particulate air pollutants can be controlled for with an HVAC system and filters.

Air quality in display areas is of significant importance for preventative conservation of
art. Construction and decoration materials for exhibitions and showcases are often contributors to poor indoor air quality.⁶ For conservation of artwork, museums substitute specific raw materials known for corrosive emissions, such as wood-based products or felt and acid-curing silicone rubbers, with inert products that have low emissions.⁶ Air pollution can also cause pigments in feathers and ethnographic objects to fade.⁷

It is important to utilize the correct materials for shelves and cabinets in display cases. Metal is a preferred material for storage and display because it is inert, nonflammable, and does not emit harmful vapors; however, metal shelves can be susceptible to rusting, so they should be covered by a protective enamel layer.⁵ Wooden shelves emit harmful vapors such as formic acid and peroxides, and should be sealed with a sealant or barrier foil.⁵ These paint-on sealants should be water-based polyurethane sealants, acrylic latex emulsions, or epoxy-resins.⁵ Barrier foils are impermeable to gases and are inserted between two layers of inert plastic.⁵ Glass cases in these museum environments should be scratch resistant, gas impermeable, and have UV-light filters.⁵ The display of collections is just as important as the storage of those items. Exhibit cases need to be made of inert materials to prevent off-gassing from harmful substances given off by some types of wood.¹ Generally, adhesives should not be used to mount artifacts, and the display should provide the least stress on the artifact as possible.¹ All of these factors are vital contributors to preserving artifacts in a museum setting.

**Volatile Organic Compounds**

Volatile organic compounds, or VOCs, are hydrocarbons that are in a gaseous state at ambient temperatures.⁷ Sources of VOCs can range from solvent-based paints to varnishes and disinfectants.⁷ The United States EPA⁸ defines volatile organic compounds as “any compound of
carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.” VOCs have also been known to cause some health concerns such as eye irritation, nausea, and dizziness.⁹ Common symptoms of chronic exposure to high levels of VOCs over years to a life time include cancer, liver and kidney damage, and central nervous system damage.¹⁰

There are three types of volatile organic compounds which differ based on boiling point.¹¹ These types include very volatile organic compounds (VVOCs), volatile organic compounds (VOCs), and semi volatile organic compounds (SVOCs).¹¹ Some examples of VVOCs, SVOCs, and VOCs as well as boiling point ranges from the United States EPA are shown in Table 1.¹² Volatile organic compounds can be found naturally in materials such as wood, as well as within components of building materials, glues, furniture, and other furnishings.¹¹,¹³ Even humans visiting a museum are sources of VOCs that can be exhaled in breath and in skin emanations.¹⁴
Table 1. United States Environmental Protection Agency examples, boiling point ranges, and abbreviations for volatile organic pollutants.12

VOCs can cause harm to various types of objects. Many historically significant technologies made of rubbers and plastics have been created through the use of synthetic polymers with plasticizers and stabilizers.15 These rubbers and plastics in museum collections often show signs of degradation from storage within 5-25 years when introduced to VOCs.15 This material degradation occurs due to chemical degradation such as polymer chain scission and physical degradation such as loss of additives.15 Degradation of these objects can be evaluated through VOC emission analysis. Figure 1 shows the relationship between material degradation, damage, and VOC emission.
Figure 1. The relationship between damage to objects, VOC emissions, and material degradation.\textsuperscript{15}

Aldehydes have been indicated in damage of numerous materials such as metals, calcareous materials, and glass and enamels.\textsuperscript{7} Researchers believe that the process of aldehydes reacting to cause damage to an object occurs in a three-step process, which is illustrated in Figure 2.\textsuperscript{7} This process involves the aldehyde contaminating the atmosphere (off-gassed from display cases or construction materials), being transformed to an organic acid such as acetic acid or formic acid by the addition of an oxygen from an oxidant such as peroxide or ozone, then the organic acid harms the object chemically and loses hydrogen in the process resulting in an anion that can be identified in the damaged object.\textsuperscript{7}
Figure 2. (a) An aldehyde in the atmosphere; (b) transformation to organic acid through addition of oxygen from an oxidant; (c) damage to object occurs and causes loss of hydrogen leaving behind an anion.\(^7\)

Volatile organic compounds emitted from woods can cause environmental problems by contributing to the formation of photo-oxidants when in sunlight and nitrogen oxides.\(^{16}\) Photo-oxidants have been known to cause human respiratory tract irritation and interfere with photosynthesis, which negatively impacts forests and crops.\(^{16}\) Natural emissions of volatile organic compounds from trees are typically monoterpines, isoprene, and carbonyl compounds.\(^{16}\) The VOC isoprene (C\(_5\)H\(_8\)) reacts with nitric oxides (NO\(_x\)) to contribute to the formation of ozone (O\(_3\)).\(^{17}\)

Acetic acid (CH\(_3\)COOH), shown in Figure 3, is a known VOC emitted by hardwoods such as oak, cherry, and beech.\(^3\) Acetic acid can cause damage to objects it surrounds when it becomes volatile, and has been show to cause harm to museum artifacts due to storage conditions.\(^5\) Acetic acid has been indicated by numerous studies to be a major contributor to museum artifact contamination and damage.

Figure 3. Chemical structure of acetic acid
Museum Artifact Damage

Materials encased in wood have been known to experience damage due to acetic acid emitted from the wood.\textsuperscript{18} The source of acetic acid in wood comes partly from the hydrolysis of acetyl group esters in the hemicellulose, which makes up approximately one-third of the carbohydrates in the wood.\textsuperscript{18} Wood has been known to contribute to the corrosion of metals, specifically to museum artifacts in direct contact with or stored in specific kinds of woods.\textsuperscript{19} Corrosion is due to oxidation and occurs when there is moisture and oxygen interacting with a metal.\textsuperscript{20} For example, the overall reaction for the corrosion of iron in the presence of oxygen and water is shown in Figure 4. The cause of damage to these museum artifacts is often from corrosive vapors that are emitted from the storage container or objects stored together.\textsuperscript{19,21} Raising temperatures of wooden storage boxes will increase humidity and, therefore, lead to corrosion.\textsuperscript{19} In addition to moisture, woods can emit volatile organic molecules such as carboxylic acids.\textsuperscript{19} Metals can undergo corrosion when in contact with volatile acids such as acetic acid. It is important to have storage conditions that protect from dust, outward contaminants, and humidity, while not emitting corrosive vapors.

Acid corrosion of metal is caused by an electrochemical process.\textsuperscript{22} Metal corrosion typically requires a potential difference at points on the corroding surface, a mechanism for charge transfer between conductors, and a continuous path from cathodic and anodic centers.\textsuperscript{22} Figure 5 illustrates the corrosion process of iron and the cathodic and anodic sites on the surface. This corrosion involves the diffusion of moisture, oxygen, and the acidic pollutant to the surface.
Figure 4. The overall reaction for the corrosion of iron in the presence of oxygen and water.$^{21}$

\[
2\text{Fe}(s) + \text{O}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{Fe(OH)}_2
\]

Figure 5. The corrosion of iron in the presence of oxygen and water with the anodic and cathodic sites on the surface of the metal indicated.$^{23}$

As seen in Figure 6, lead in artifacts is often heavily susceptible to corrosion from storage conditions, and in this case the inscribed lead plate was stored in a glass case that included wooden relics. Figure 7 shows another example of damage occurring due to storage with wooden material. This brooch displays white corrosion of cellulose acetate-nitrate. Severe corrosion due to acetic acid damage of lead historical museum objects can be seen in Figure 8. Some of the figurines in Figure 8 are broken and unrecognizable due to the acetic acid damage. Acetic acid can cause damage on a variety of metals as seen in Figure 9. Acid vapors from the wood can cause varying degrees of corrosion to metals such as steel, zinc, cadmium, copper, and brass.$^{24}$
Figure 6. An inscribed lead plate from the Bishop Absalon’s grave in the Monastery Church at Soro, Denmark. The artifact was stored in a brass and glass box with oak wood relics. Air and moisture interacting with the oak wood in the case caused corrosion of the artifact.\textsuperscript{19}

Figure 7. A coral brooch and ornaments of cellulose nitrate were stored in an oak barrel for many years causing white corrosion of cellulose acetate-nitrate.\textsuperscript{19}
Figure 8. (a) A lead statue heavily damaged by acetic acid. (b) Figurines have undergone corrosion as a result of acetic acid from the wooden display board.\textsuperscript{7}

Figure 9. The effect of acetic acid concentration in ppm on metals from a study on corrosion of metals by acid vapors from woods by Clarke and Longhurst. (A) Steel, (B) Zinc, (C) Cadmium, (D) Copper, (E) Brass.\textsuperscript{24}
Evolved Gas Analysis and Titrations

Evolved gas analysis, or EGA, is an analytical method in which VOCs can be identified and quantified as a function of controlled changes in temperature. In order to determine which gas is being evolved, EGA is typically coupled with mass spectrometry or gas chromatography. Mass Spectrometry is a technique that can identify and quantify an analyte by measuring the mass-to-charge ratio of ions. In gas chromatography chemicals are separated and identified based on differences in properties, allowing movement through a mobile and stationary phase at different times.

Titrations are used to determine the concentration of an analyte by adding a solution of known concentration and letting the reaction reach neutralization. The analyte is typically dissolved in a solution and an indicator is added, commonly phenylalanine for titrations with a strong acid or base (in our case, base); and a reagent is titrated into the analyte and indicator solution. When the analyte solution changes color, the amount of acid or base used is recorded and the unknown concentration of the analyte can be calculated.

This study utilized evolved gas analysis and titrations to measure acetic acid present in various hard woods. The correlation between the data collected by two methods was then evaluated. The quantification of acetic acid in these wood samples will help to better inform and improve future museum artifact storage.
Materials and Methods

Evolved Gas Analysis Method

The calibration curve was created utilizing an Agilent Technologies 6890N GC-FID equipped with a homemade EGA oven inlet. Acetic acid was dissolved in acetone to a known molar concentration. Aliquots of this solution were added to the EGA cup containing a glass filter and analyzed by GC-FID. Analyses were performed in triplicate. Peak areas were determined and a calibration graph of peak area versus nanomoles of acetic acid was created.

The wood samples red oak, thick plywood, medium density fiberboard, thin dark stained plywood, red elm, cedar, and coffee nut were attained from Northwest Lumber in Indianapolis, Indiana and were shaved down to uniform samples of approximately 8 mg and analyzed by evolved gas analysis. The method utilized a one minute injection time. The wood samples were analyzed in triplicate with four injections each in order to attain the nanomoles of acetic acid per milligram of wood sample. Figure 10 shows the wood shaving process and evolved gas analysis equipment.

Titration Method

A titration method was performed in order to assess correlation between amounts of acetic acid from the evolved gas analysis. The method utilized 2 grams of shaved wood sample in 20 mL of deionized water and left to sit for a week. Figure 10B shows the wood sample container and 20 mL of deionized water used. An additional 20 mL of deionized water was added to this solution prior to titration. 10 mL of the solution was then titrated with 0.01 M sodium hydroxide and phenylalanine in order to determine the concentration of acetic acid. The data collected from this method was then compared to the evolved gas analysis method through statistical analysis with F and T tests.
Figure 10. (A) Wood shaving setup including razor for fine shaving of samples. (B) Titration preparation of 2 grams of red oak wood in 20 mL of deionized water. (C) Homemade EGA cup and hook for sample injections in the oven inlet. (D) Agilent Technologies 6890N GC-FID equipped with a homemade EGA oven inlet.
Results and Discussion

With the current calibration curve for the EGA method, red oak, thick plywood, and red elm were above the limit of detection. With this evolved gas analysis calibration, MDF had signals below the limit of detection, meaning we could not detect acetic acid with confidence. The acetic acid concentrations obtained for MDF wood samples cannot be accepted with confidence due to being below the limit of detection. Thin dark plywood, cedar, and coffee nut samples had signals below the limit of quantitation and are represented as semi-quantitative data in Table 2. Figure 11 shows the calibration curve for the evolved gas analysis method.

Figure 11. A calibration curve of nanomoles of acetic acid versus peak area attained from evolved gas analysis.

Of the wood samples analyzed that were above the limit of quantitation on the EGA calibration curve, the red oak was found to have the highest acetic acid concentration, followed by thick plywood, and then red elm. No acetic acid was detected in medium density fiberboard
(MDF) with the evolved gas analysis method. Table 2 shows levels of acetic acid found from both methods as well as statistical analysis of precisions and differences between means. From statistical analysis with T-tests, it was found that the EGA method and Titration method provided statistically similar means of acetic acid concentrations in the woods red oak, thick plywood, red elm, cedar, and coffee nut; this means that any difference between the averages of these methods can be attributed to chance. The mean acetic acid concentrations for thin dark plywood from the EGA and titration methods were found to be statistically different, meaning there was a difference in averages from the two methods for this wood sample. When precisions of the two methods were compared using an F-test comparing standard deviations of the triplicate samples, all wood types except MDF, which was not detected for EGA, were found to have statistically different precision. This F-test was comparing the variance of data points between the two methods for each wood sample.

The evolved gas analysis method posed a few challenges. The cup and hook made injections of samples difficult when the cup fell into the system due to mechanical error; the procedure would then have to be redone. The titration method utilized a simpler preparation and took less time to perform than the EGA method. Excluding the preparation time for the titrations, all titrations could be performed in approximately three hours, which was a significantly shorter amount of time than the EGA method, which only allowed for the analysis of one to two of the triplicate runs of wood sample per day. If the EGA was equipped with an auto-sampler this method could be performed more easily as well. Because the titration method was less time consuming than the evolved gas analysis method, it would be the preferred method for further studies based on preparation time. The titration method is excellent for quantifying acetic acid,
but it may not necessarily be detecting volatile acetic acid only and could be detecting acetic acid from a different mechanistic pathway other than volatility.

The red oak, red elm, and thick plywood should be prohibited from the museum environment due to higher concentrations of acetic acid vapors being emitted. The cedar, coffee nut, and dark stained plywood were below the limit of quantitation and would require further evaluation in order to determine concentration of acetic acid with confidence. For MDF, which showed signals below the limit of detection, more research would be needed to assess levels of acetic acid since our methods could not detect any with confidence.

Future research should evaluate many types of hardwoods, and attempt other evolved gas analysis methods such as an evolved gas analysis coupled with mass spectrometry. Many of the hardwoods from this small sample showed volatile acetic acid and if used in a museum could negatively affect the objects that are sharing the same environment. Ideally, museums should prohibit the use of woods with any amount of acetic acid within because it is a highly volatile organic compound.
Table 2. Concentration of acetic acid in nmol/mg found in various wood types from a titration method and an evolved gas analysis method. Wood samples below the limit of quantitation are represented as semi-quantitative data with asterisks.

<table>
<thead>
<tr>
<th>Wood Type</th>
<th>Titration (nmol/mg)</th>
<th>EGA (nmol/mg)</th>
<th>Tcalc</th>
<th>Fcalc</th>
<th>Ttable</th>
<th>Ftable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Oak</td>
<td>2.13 ± 0.2</td>
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<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
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<tr>
<td>Thin Dark Plywood*</td>
<td>4.88 ± 0.2</td>
<td>None Detected</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
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<tr>
<td>Thick Plywood</td>
<td>3.23 ± 0.1</td>
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<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
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<tr>
<td>MDF</td>
<td>5.12 ± 0.2</td>
<td>None Detected</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
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<tr>
<td>Coffee Nut*</td>
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<td>N/A</td>
<td>N/A</td>
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</tr>
<tr>
<td>Cedar*</td>
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<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
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</tr>
<tr>
<td>Red Elm</td>
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<td>N/A</td>
<td>N/A</td>
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</tr>
<tr>
<td>Thin Dark Plywood*</td>
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<td>Thick Plywood</td>
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<tr>
<td>MDF</td>
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<tr>
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<tr>
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<tr>
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<td>N/A</td>
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</table>

Quantitative data with asterisks. T values and F values are shown to evaluate statistical means and precisions.
References


