Haddon Dine
Winterthur/University of Delaware Program in Art Conservation
Supervisors: Lauren Fair, Dr. Jocelyn Alcántara-García, Lara Kaplan

A 19th-Century Aquarium:
How Collaboration Informed the Technical Study and Treatment

INTRODUCTION

Winterthur has an unusual 19th-century aquarium consisting of a splash pan, octagonal tank, and a central architectural structure (fig. 1).

Fig. 1. Overall front view of the aquarium before treatment. Winterthur Museum, Garden & Library. Dimensions: overall height: 23.74 in. (60.30 cm), overall width (diameter): 22.13 in. (56.20 cm). Bequest of Henry Francis du Pont 1965.2192

The object is constructed primarily of painted tinned iron, galvanized iron, and glass, with mirrors, silk curtains, glass and wood fish, pebbles, and faux plants[1]. While the octagonal shape of the tank was common for aquaria, there are no known comparables for this object as a whole. It is not known if the Winterthur object was constructed to function as an aquarium or for decorative purposes only. It is possible that the pieces are not original to one another and were assembled as a decorative object, perhaps using an aquarium tank.

Working with the Winterthur scientists and Winterthur objects conservation supervisors, I conducted a technical examination and conservation treatment on this aquarium during my second year in the Winterthur/University of Delaware Program in Art Conservation (WUDPAC). This work was done in parallel to the research of Rebecca Duffy, a second-year fellow in the Winterthur Program in American Material Culture (WPAMC), who wrote her thesis on 19th-century parlor aquaria. There is a lack of current historical scholarship on these objects, and there are not many on display in museum collections. Rebecca Duffy's thesis "The Age of Aquaria: The Aquarium Pursuit and Personal Fish-Keeping, 1850-1920" investigates how aquaria functioned as decorative objects, natural history collections, and also containers of household pets. She researched aquarium makers and sellers and tracked down examples of 19th century aquaria. Her scholarship allowed interesting discussions on the context of the aquarium, and influenced sampling, analysis, and interpretation of results for the technical study.

HISTORICAL BACKGROUND

I knew nothing about 19th-century parlor aquaria before seeing this aquarium at the start of my second year. Rebecca Duffy had at this point been researching aquaria for roughly a year, and she shared with me what she had learned and directed me to sources.

Keeping ornamental fish has been a practice since ancient times (Hamera 2011, 3-4). The 19th-century aquarium, ideally an almost self-sustaining aquatic ecosystem, is viewed as having evolved from the Ward Case, an airtight glass container for growing ferns (Hamera 2011, 3-4;

[1] For a more in-depth description of the object, the "Conservation Treatment Report" is on file at Winterthur.

Brunner 2005, 30-37). This can be said to have grown out of a combination of influences, including scientific study of creatures and plants, the evolution of the cabinet of curiosities, and the changing fads of collecting things (Brunner 2005, 17-18).

There was a growing popularity of parlor aquaria in the 19th century (Duffy 2017). Englishman Philip Henry Gosse is credited with much of the popularization of the aquarium (Brunner 2005, 38). There was an aquarium fad in the United Kingdom from roughly 1850-1875, and this fad spread to the United States (Duffy, pers. comm.). Tank size and shape was quite variable, and framing material varied, including wood, zinc, and iron (Hamera 2011, 14). Octagonal tank aquaria were not unusual (fig. 2), but an aquarium with a central architectural feature such as the Winterthur one is. Rebecca Duffy has not found any comparable examples. Duffy thinks that our Winterthur aquarium is likely one-of-a-kind. One possible explanation for our aquarium is that it was made by a metalworker to show off their skill.

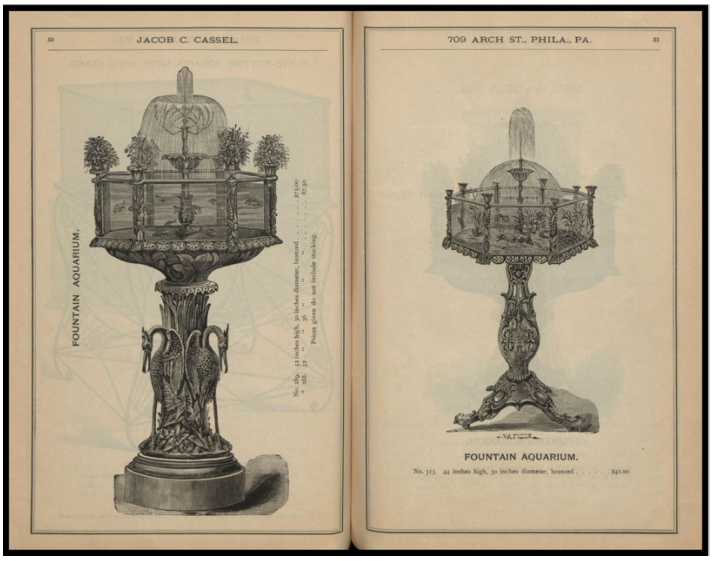


Fig. 2. Pages from Cassell's Fair-Hill Terra Cotta Iron Works trade catalogue, showing Fiske aquaria with fountains. These aquaria manufactured by J. W. Fiske are examples of octagonal aquaria.
Courtesy of the Winterthur Library: Printed Books and Periodical Collection

Armed with this historical background on aquaria, we began formulating questions for the technical study.

FORMING QUESTIONS FOR THE TECHNICAL STUDY

The collaboration with Rebecca Duffy greatly influenced the technical study. Two main questions were: are the pieces of the aquarium original to one another? And, was this object actually intended to function as an aquarium and hold water or was it just decorative? We also wanted to more thoroughly characterize and understand the materials and construction.
A review of the literature did not encounter any analytical studies of aquaria, but there have been analyses on similar/relevant materials. Additionally, there is extensive literature on the manufacture of some of the materials used in the construction of the aquarium, which provided much relevant information when it came to interpreting analyses.[2]

Techniques used in the analysis of this aquarium included: examination in ultraviolet light, x-ray fluorescence (XRF), cross-section microscopy, scanning electron microscopy – energy dispersive spectroscopy (SEM-EDS), Fourier Transform infrared spectroscopy (FTIR), gas chromatography mass spectrometry (GCMS), Raman spectroscopy, and x-ray diffraction (XRD).

TECHNICAL STUDY – ARE THE PIECES ORIGINAL TO ONE ANOTHER?

Examination and History

The start of the investigation was examination, while also looking into the history of this particular aquarium. Rebecca and I agreed on terms for the sections of the aquarium. There is the architectural structure, which consists of an eight-sided pavilion and a four-sided building. This structure sits in the tank, which is attached to the pan (fig. 3).

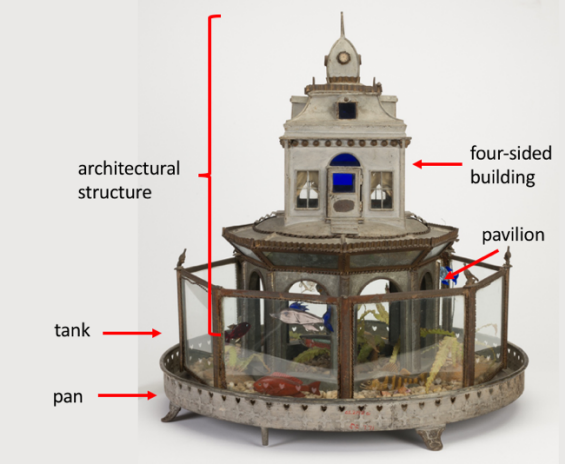


Fig. 3. Terms for the different sections of the aquarium.

[2] For further material background and literature review, see the "Conservation Treatment Report" and "Technical Examination of a 19th Century Aquarium (1965.2192A,B)", both on file at Winterthur.

After this, I diagrammed the sides with numbers. The numbers I used were numbers we found penciled on the base of the pavilion. These same numbers were applied to the tank sides. For example, the side of the tank lined up with Side 6 of the pavilion was Side 6 of the tank. There are four doors on the four-sided building and only one is hinged, so the side with the only hinged door is referred to as the front (fig. 4).

This aquarium was purchased by H. F. du Pont from George McKearin in 1948; McKearins Antiques was located in Hoosick Falls, NY (Winterthur Correspondence Record). From a photo sent to Mr. du Pont by McKearin, during their correspondence before the purchase, we can tell that the fish, plants, and pebbles were added some time after the aquarium came to Winterthur (fig. 5). These components are considered original to the du Pont era and were treated with the rest of the object, but they were not considered in the technical study.

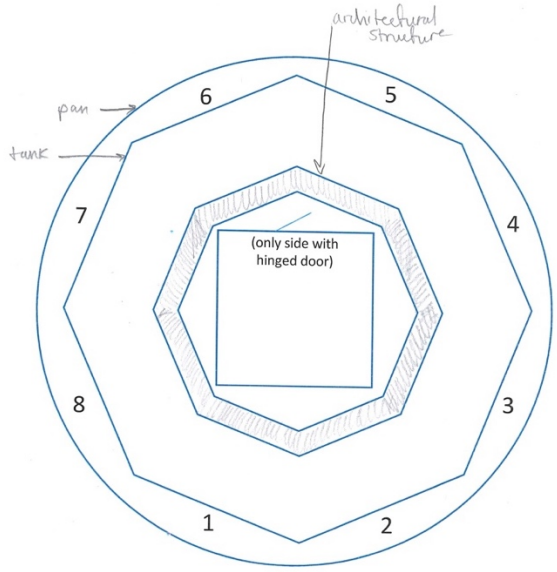


Fig. 4. Numbering system. Tank and pavilion sides referred to by penciled numbering system found on the base of the pavilion. The front of the four-sided building is designated as the side with the hinged door.

Fig. 5. Photo from George McKearin, the dealer that du Pont purchased the aquarium from. The fish, pebbles, and plants are absent, indicating they were added at Winterthur. (Orientation of pavilion to tank is offset.)
Courtesy, Winterthur Museum, Aquarium, 1840-1880, England or United States, Tinned sheet Iron, Bequest of Henry Francis du Pont, 1965.2192

Metal Tabs

In order to examine and treat the object, it had to be disassembled. Because of Rebecca Duffy's interest in the construction and assembly of this object, she joined my supervisor Lauren Fair and me for the disassembly. The architectural structure lifted out, and then we removed the plants, fish, and pebbles (fig. 6).

Fig. 6. Disassembling the aquarium with Rebecca Duffy and Lauren Fair. Photo credit: Lara Kaplan

When we removed the pebbles we found metal tabs in the bottom of the tank (fig. 7). Only one was still attached, a second was detached, and the other six are missing, with only solder remnants marking where they were.

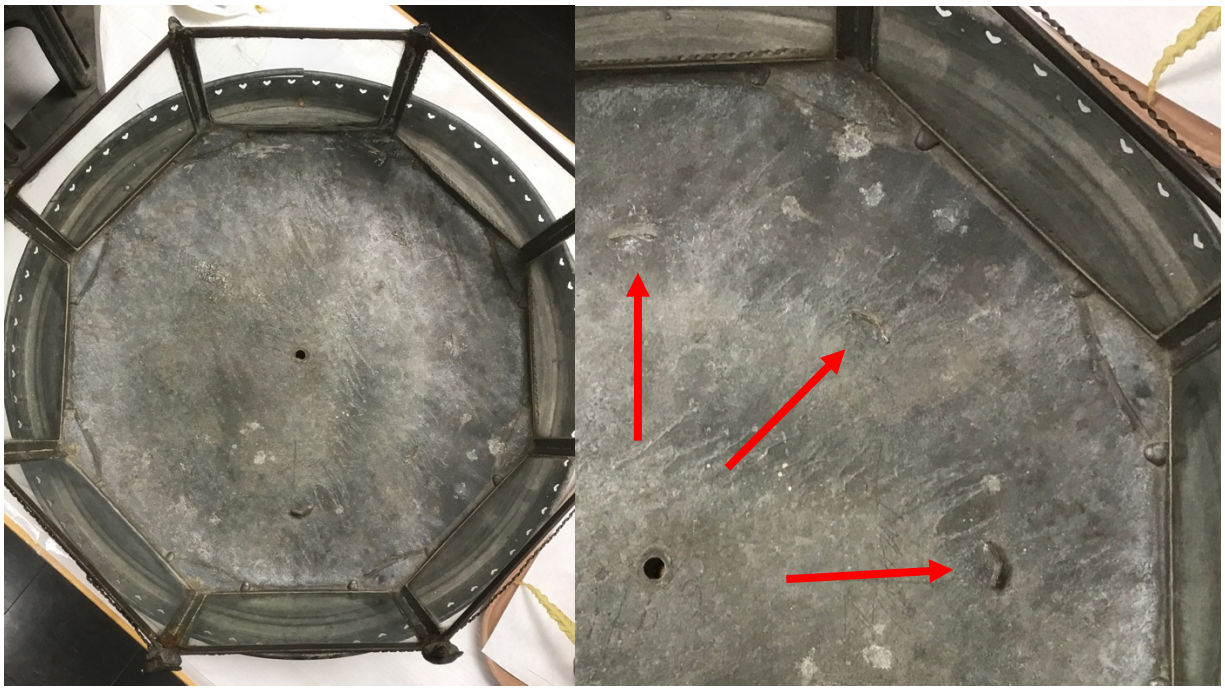


Fig. 7. Overall view of inside of tank (left) and detail (right) with arrows pointing at the one attached tab and two areas of solder where tabs used to be.

It seems that these tabs either fit just inside, or just outside, the corners of the base of the pavilion. This would put the corners of the pavilion in the centers of the tank panes. The sides of

the pavilion would not be parallel to the tank sides, as they were most recently displayed (fig. 1). The 1948 photo of the aquarium from the antique dealer shows the pavilion offset, and sitting inside two of these tabs (fig. 5). There is an undated photo in the Winterthur object file in which the sides are parallel (fig. 8). Due to the absence of the glass fish, that photo is likely earlier than a 1979 photo that shows the architectural structure offset again (fig. 9). It seems the orientation was changed over the years.

Fig. 8. Undated photo in Winterthur object file, with the architectural structure in the parallel configuration.
Courtesy, Winterthur Museum, Aquarium, 1840-1880, England or United States, Tinned sheet Iron, Bequest of Henry Francis du Pont, 1965.2192

Fig. 9. 1979 photo of the aquarium, with the architectural structure in the offset configuration. Courtesy, Winterthur Museum, Aquarium, 1840-1880, England or United States, Tinned sheet Iron, Bequest of Henry Francis du Pont, 1965.2192

The tabs suggest that the pieces go together, but the tabs could have been added later. It is possible that the architectural structure and tabs were added to modify an existing aquarium tank. It is inconclusive whether the pieces of the aquarium are original to one another. If this was known, it would have large implications for the question of whether the object was intended to hold water.

TECHNICAL STUDY - WAS THE AQUARIUM INTENDED TO HOLD WATER?

Spouts

On the bottom of the aquarium, there are two things that seem to possibly be drains or spouts (fig. 10). The one in the center is part of the tank, and a hole was cut in the pan to accommodate it. The similar spout on the edge of the pan is integral to the pan. It is possible that there was a fountain in the tank, such as in the Fiske aquarium (fig. 2). Another possibility is that these spouts were part of a water circulation system.

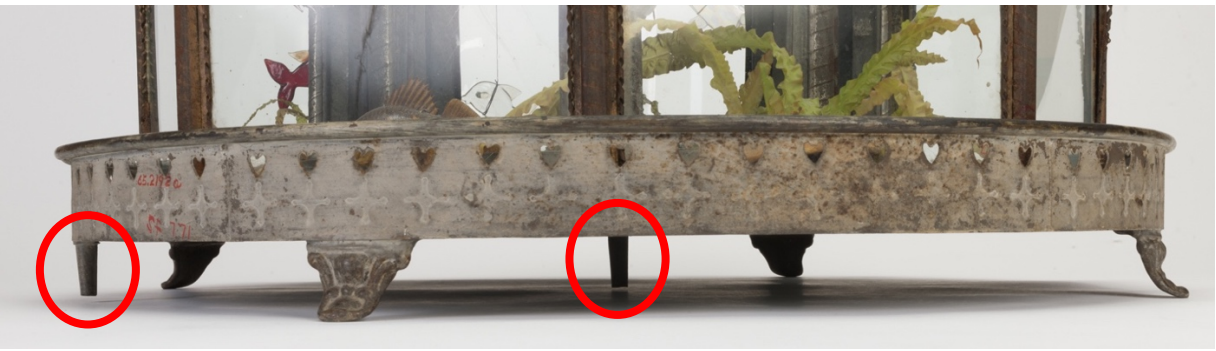


Fig. 10. View showing the "spouts/drains" on the pan, which are circled in red.

If this object did have a fountain, it seems unlikely that the architectural structure always sat where it does now, making it unlikely that the current configuration is original.

Potential Tank Sealant

A major step in the investigation of whether this held water was looking for sealant. Rebecca Duffy found during her historical research that an aquarium intended to hold water would likely have had lead putty as a sealant. In his 1855 book on aquaria, Philip Henry Gosse mentions setting glass into grooves in slate and wood with "white-lead putty" (Gosse 1855, 5). He quotes W. Dodgson on setting glass in white lead, and then coating the white lead with "shell-lac dissolved in naphtha and made into a paste with whiting" (Gosse 1855, 6). The composition is likely similar to or the same as what was used in windows. Window putty was used to seal the gaps between glass and frame in windows to keep out rain and air. It could include calcite, white lead, and linseed oil. [3]

[3] Tegethoff quotes an 18th century recipe describing the putty: "Parisian window putty is produced in the following manner: 7 pounds of linseed oil, together with 4 ounces of ground umber, are intensely boiled; and while this is still hot add 2 ounces of yellow wax and reheat everything once again. And then knead in 5 ½ pounds of ground white

A sample of the material between the tank panes and framing (fig. 11) was analyzed. Results from both Fourier Transform Infrared Spectroscopy (FTIR)[4] and Raman spectroscopy[5] suggested the presence of barium sulfate. Gas chromatography mass spectrometry (GCMS)[6] resulted in peaks for azelaic, palmitic, and stearic acids, suggesting a drying oil (such as linseed oil). The sample was also analyzed using x-ray fluorescence spectroscopy (XRF)[7], which at first detected mostly lead and zinc, with iron and calcium. Flipping the sample and taking a spectrum from the other side gave a different result, detecting barium, more zinc, and less lead. This seems to confirm the presence of barium sulfate, although it could be contamination. Both XRF spectra confirmed the presence of lead and calcium.

Fig. 11. Inside the tank. Area of sampling of tank putty is circled in red.

Both the drying oil binder and the presence of lead in the tank sealant are consistent with literature for aquarium sealant and window putty. However, this still does not determine whether the aquarium was intended to be watertight, as window putty may have been used simply to keep the panes from shifting.

---

chalk and 11 pounds of lead white" (Rohleder 2014, 143). Later, less lead was used, and more chalk; Tegethoff quotes an 1836 recipe including "linseed-oil varnish (linseed oil boiled with red lead or lead oxide)" kneaded with chalk (Rohleder 2014, 143). An ICON article discussing removal of cement applied to stained glass as part of a restoration campaign after WWII explains that the cement was a mixture of calcium carbonate, linseed oil, red lead as a hardening agent, and lamp-black pigment to darken it (Thomas 2015).

[4] Sample material was rolled flat on a diamond cell with a steel micro-roller. The sample was analyzed using the Thermo Scientific Nicolet 6700 FT-IR with Nicolet Continuμm FT-IR microscope (transmission mode); data was acquired for 128 scans from 4000 to 650cm^{-1} at a spectral resolution of 4cm^{-1}. Spectra were collected with Omnic 8.0 software and analyzed in this program with various IRUG and commercial reference spectral libraries. Analysis was conducted with Dr. Jocelyn Alcántara-García.

[5] The sample was analyzed with the Renishaw Invia Raman spectrometer (785nm diode laser or 514nm argon ion laser) in conjunction with WiRE 3.4 software with extended scan from 200-2200cm^{-1}, 50X objective lens, exposure time of 10-20 seconds/scan for 3 accumulations, and 5 % laser power. Analysis was conducted with Dr. Jocelyn Alcántara-García.

[6] Samples were treated with 1:2 MethPrep II reagent in benzene. Samples were analyzed using the Agilent Technologies 7820 gas chromatogram equipped with Agilent 5975 mass selective detector (MSD) and an automatic liquid injector. A sample volume (splitless) of 1μL was injected onto a 30m × 250μm × 0.25μm film thickness HP-5MS column (5% phenyl methyl siloxane at a flow rate of 1.5mL/minute). The Agilent Technologies G1701EA GC/MSD ChemStation Control software was used. Chromatograms and mass spectra were interpreted using the Agilent MSD Enhanced Chemstation Data Analysis software with NIST MS Search 2.0 database. Sample prep was done with Catherine Matsen. Analysis was conducted by Dr. Chris Petersen.

[7] Analysis was performed with an ARTAX μXRF spectrometer using a rhodium tube (600 μA current, 50 kV voltage, 100 seconds live time irradiation, approximately 70-100 micron spot size) with element detection range of potassium (K) to uranium (U). Analysis was conducted with Dr. Jocelyn Alcántara-García.

Potential Pavilion Coating

If the tank was filled with water, the pavilion (the lower portion of the architectural structure) would have needed a protective coating. Examination in ultraviolet light revealed a coating that fluoresced on the pavilion. Samples were taken from a column and the galvanized arches. Analysis by FTIR and GCMS suggested the presence of a drying oil.[8] This coating would likely not have held up in water. Additionally, it does not seem that the coating is applied over the entire surface of the lower portion of the pavilion.

TECHNICAL STUDY – DID WE SOLVE THE MYSTERY?

The two questions must be discussed together to attempt to come to a conclusion. If the pavilion was originally intended to sit in the tank where the tabs are, then perhaps this object was not meant to actually function as an aquarium. Another possible explanation is that the tank is from an actual aquarium, meant to hold water, and it was modified later with the tabs when the architectural structure was added. Additionally, it is of course possible that the pieces are not original to one another and no portion of the object was intended to hold water.
We feel fairly comfortable saying that this object does not seem to have held water in its current arrangement. As it exists, it is decorative.

TECHNICAL STUDY - FURTHER MATERIAL INVESTIGATION

The technical study aimed to characterize the materials of the object, and while much of this helped inform the two questions discussed above, other investigations simply resulted in interesting identifications or had treatment implications.

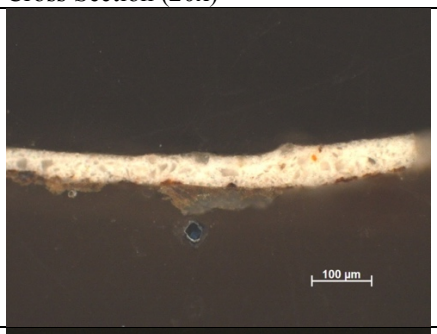
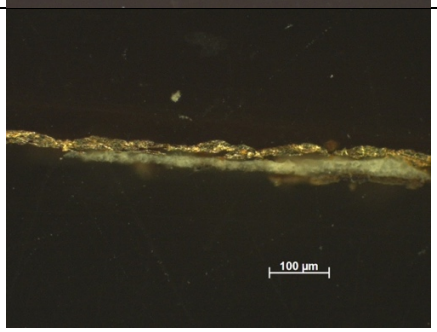
Cross Section Analysis of the Paints

Cross sections of the grey and metallic paint on the aquarium were taken to determine the stratigraphy through microscopy (see Table 1), and also to allow elemental analysis by scanning

[8] Analysis procedures as listed above. FTIR conducted with Dr. Jocelyn Alcántara-García. GCMS analysis conducted by Dr. Chris Petersen.

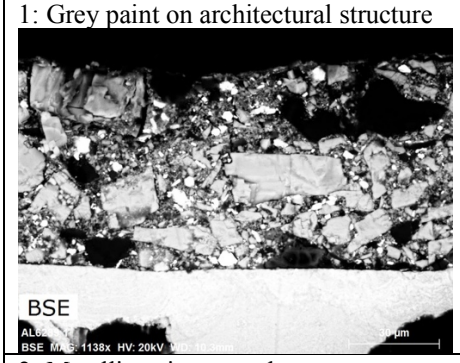
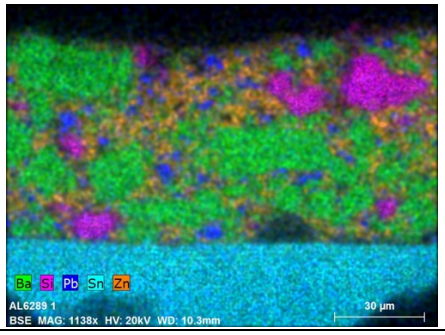
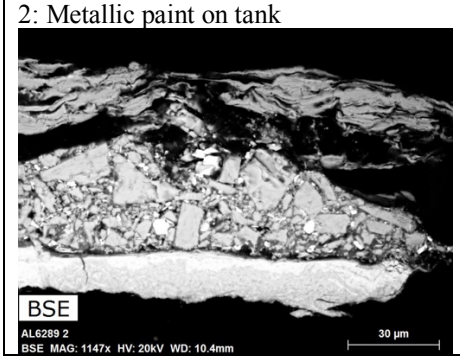
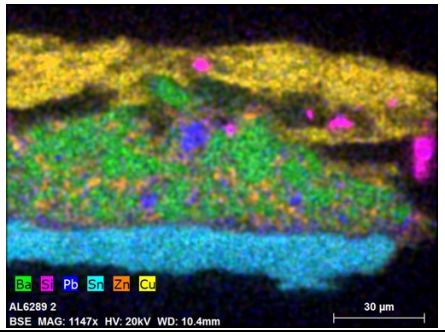
electron microscopy with energy dispersive spectroscopy (SEM-EDS)[9] to determine the composition of the pigments (see Table 2). GCMS was also used to identify the binder of the grey paint. Peaks for the methyl esters of azelaic, palmitic, and stearic acids suggest a drying oil such as linseed oil (Petersen 2017 pers. comm.; Mills and White 1994).

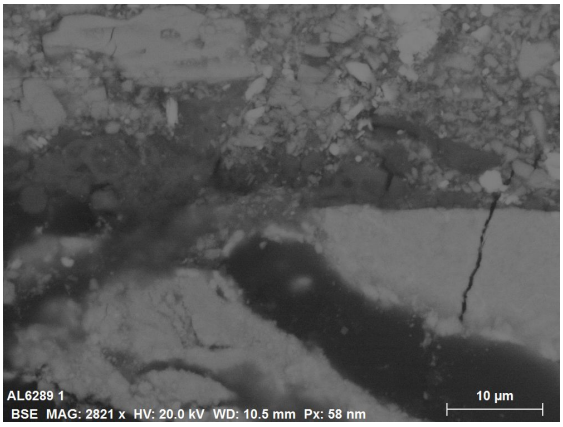
Table 1. Grey and metallic paint samples taken for cross-section analysis

Sample Number	Sample Description	Sampling Location	Normal Light Photomicrograph of Cross Section (20x)	Layers
Sample 1	grey paint, from proper right side of building, dormer window, edge just above blue glass			• Grey paint • particles of tin
Sample 2	gold/bronze-colored paint, from Side 1 of the octagonal tank, upper right edge			• Metallic flake paint • Possible size layer? • Paint layer with similar appearance to paint in Sample 1 • particles of tin

[9] Cross-sections were examined using a Zeiss EVO MA15 scanning electron microscope with LaB_6 source at an accelerating voltage of 20kV for the electron beam, working distance of approximately 10mm, and sample tilt of 0°. The EDS data was collected with the Bruker Nano X-flash® detector 6 | 30 and analyzed with Quantax 200/Esprit 1.9 software. Analysis conducted with Catherine Matsen.

Table 2. Elemental Analysis Results from SEM-EDS on cross-sections of paint

Sample Number and Backscatter electron image	False Color EDS Map	Elemental Results	Identification
1: Grey paint on architectural structure 		Grey paint layer: Ba, Si, Pb, Zn, and some Ca, Si, Al. Tin on the bottom	zinc white (zinc oxide) with barium sulfate, or lithopone (zinc sulfide coprecipitated with barium sulfate).
2: Metallic paint on tank 		Metallic flake layer: Cu and Zn Paint layer: Ba, Zn, Pb Tin on the bottom	The metal is brass (copper and zinc) – bronze powder paint. The paint layer appears similar to the paint in Sample 1.



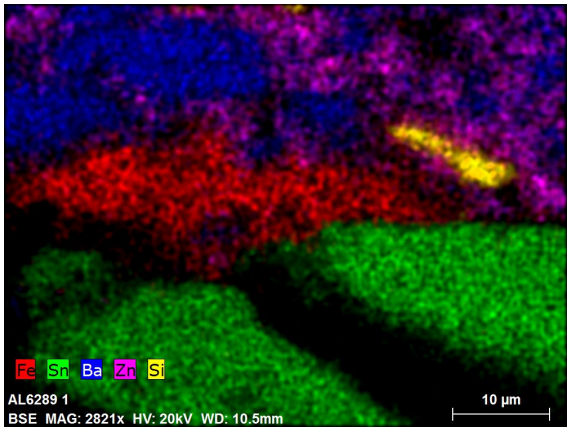


Fig. 12. Secondary electron image (left) and false color elemental map (right) of an area that appeared red in normal light photomicrographs at the interface between the grey paint layer and the tin in Sample 1. The red area was presumed iron corrosion, which is confirmed by the analysis.

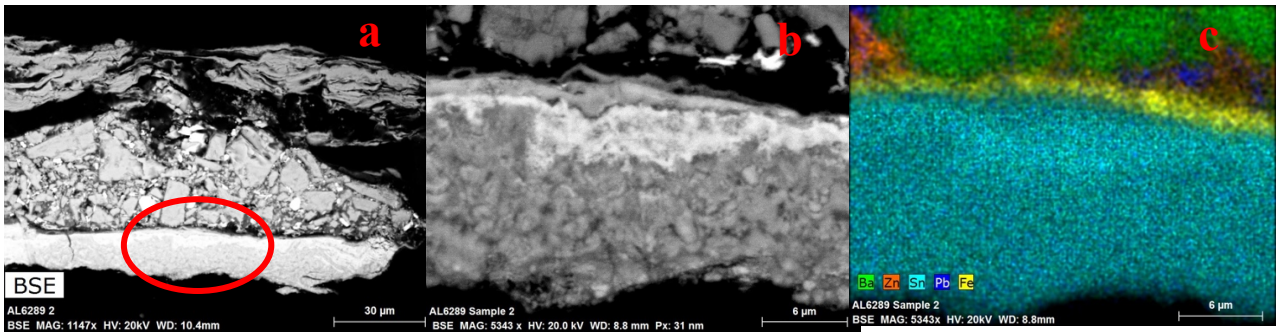


Fig. 13. Backscatter electron image (b) and false color elemental map (c) of an area of Sample 2 (circled in a) with a layered appearance in the tin. There is a layer of iron above the tin (yellow in the EDS map) but no elemental explanation for the difference in appearance of the tin layers. It may be a difference in concentration.

The elemental analysis of the grey paint from the pavilion (Sample 1, Table 2) by SEM-EDS indicates zinc white (zinc oxide) with barium sulfate, or lithopone (zinc sulfide coprecipitated with barium sulfate). The particles are separated enough that it seems like barium sulfate with zinc white, not lithopone (Matsen 2017). The silicon is possibly from a clay filler (also the aluminum), but the silicon is also possibly from polishing the cross sections with Micro-Mesh®.

SEM-EDS elemental analysis of the metallic flake in Sample 2 (see Table 2) identified copper and zinc, suggesting that the metallic pigment is brass. Sample 2 also contains a layer below the metallic layer, which appears similar in composition to the grey paint in Sample 1. The layer of grey paint below the metallic paint in the cross section taken from the tank is interesting, as it raises the question of whether the metallic paint was added in a later campaign than the grey paint. The presence of what seems like grey paint below the metallic paint may inform the discussion of whether the tank and architectural structure are original to each other. Perhaps a thin layer of the grey paint was applied as a preparatory layer to the metallic paint.

There are areas of iron in both cross sections, probably corrosion coming up from below the tin (figs. 12 and 13).[10]

[10] There has been much research on the corrosion of tinplate used in the food industry. The containers are usually steel and most of the research is focused on the effects of food products, so these are not immediately relevant to the current study. However, there are discussions of the iron tin alloy between the base metal and the tinning, and the corrosion resistance of the top tin layer (Zumelzu et al. 2003).
There has also been analysis of oil paintings on tinplate, which is perhaps more relevant to this aquarium study. In a 2010 analysis of a Portuguese artist's paintings on tinplate, portable x-ray fluorescence (XRF) was used to identify pigments and fillers in the paint, and scanning electron microscopy with energy-dispersive spectroscopy (SEM-

The cross section samples both had bits of tin on the bottom of the samples. This is likely tin oxide. Catherine Matsen found in her 2007 cross-section analysis of tin-coated stainless steel[11] that there was a slightly darker friable layer above the tin layer, which contained tin when analyzed by SEM-EDS. Matsen stated that though Raman would be necessary to confirm tin oxide, the layer was likely tin oxide. It seems likely that if the bits of tin in the aquarium sample were pulled along with the sampled paint, they were probably crumbly tin oxide as well.

Attempts to characterize what appeared to be layers in the tin on the bottom of the Sample 2 cross section (fig. 13) were not conclusive, as elemental analysis shows only tin in the bulk of the metal on the bottom of the sample. Since the different layers visible are not compositionally different by EDS analysis, they are possibly different forms of tin oxide and metallic tin. Mapping of iron and tin in an area of Sample 2 showing a layered structure did reveal a layer of iron above the tin (fig. 13).

Mirrors

There are eight mirrors on the pavilion, and they show signs of deterioration. I wanted to determine whether the mirrors were mercury-tin amalgam mirrors[12] or silver mirrors.

EDX) was performed on samples of the metal support (other examination techniques including IR and UV imaging and optical microscopy were also performed) (Veiga 2010). The support was found to be steel (containing iron and carbon) coated with tin. The tin coating was irregular, and there were phosphorous and silicon oxide impurities in the steel core (Veiga 2010). The article explains that when the protective tin coating is broken, an electrochemical cell between the iron and tin is formed, with the iron acting as the anode and oxidizing. The author found migration of iron corrosion into the paint layers. In some cases, an orange tone was visible in light colored paint, and Veiga notes that the increased volume of the corrosion products can increase paint delamination (Veiga 2010). The paintings she was examining were experiencing delamination from the tinplate support in areas.

[11] Winterthur Scientist Catherine Matsen analyzed tin-coated stainless steel shingles and tin-coated iron shingles from the roof of Monticello in 2007. She performed energy-dispersive x-ray fluorescence (ED-XRF) on the samples, took cross-sections, and performed metallography and SEM-EDS on the samples. Part of the purpose of the study was to determine an explanation for rust-colored staining on the shingles and to compare restoration materials with original materials. (Matsen 2007)

[12] Using tin-mercury amalgams was the dominant method for creating mirrors from the 16th to early 20th centuries (Bright 2016). To create this kind of mirror, tin foil was laid out on a surface. Liquid mercury was brushed onto the tin. This created the amalgam. A sheet of clear glass was then laid onto the amalgam and weighted down (de Chavez 2010). The binary alloy created consists of a tin-rich solid phase and a mercury-rich liquid phase; this is inherently unstable (Arizio 2013). Over time, the mercury is slowly lost, and the solid phase grows; tin dioxide and monoxide form, and the mirror becomes less reflective (Arizio 2013).

First, x-ray fluorescence spectroscopy (XRF) was performed with the lab-based ARTAX μXRF instrument[13] (discussed above as it was used on the tank sealant). The spectra collected with the ARTAX μXRF did not identify any amalgam elements, so it was necessary to use the handheld XRF[14].

At Winterthur in 2016, Leah Bright (WUDPAC Class of 2017) performed a study on identifying mercury-tin mirrors and silver mirrors using a handheld Bruker XRF spectrometer. She compared analysis from the back and front of mirror fragments, and analyzed many mirrors in the Winterthur collection from the front. She found that while tin and mercury could be identified on the amalgam side of the mirror, only the tin was detected through the glass. Mercury peaks and tin L lines are blocked by many of the elements present in glass (Bright 2016). Bright based identification of mercury-tin mirrors on the appearance of the deterioration and the detection of tin by handheld XRF. Silver could be detected from both sides of the silver mirror fragment.

The handheld XRF spectra of the aquarium mirrors indicated tin in all eight mirrors. All eight spectra were similar (fig. 14). Based on the lack of silver and the detection of tin, the mirrors have been identified as mercury tin. They also display the characteristic deterioration of mercury tin mirrors. Further analysis of the data is needed to compare the glass composition between the mirrors as well as to the tank glass composition.

[13] Analysis conducted with Dr. Rosie Grayburn.

[14] Non-destructive, qualitative ED-XRF (energy-dispersive x-ray fluorescence) spectroscopy was performed to determine elemental composition of the mirrors on the aquarium. Analysis was performed with the handheld Bruker Tracer III-SD XRF spectrometer using a rhodium tube (40kV high voltage, 9.6μA anode current, 1 mil Ti / 12 mil Al ; 15 kV high voltage) for 100 seconds live time irradiation. Analysis conducted with Catherine Matsen.

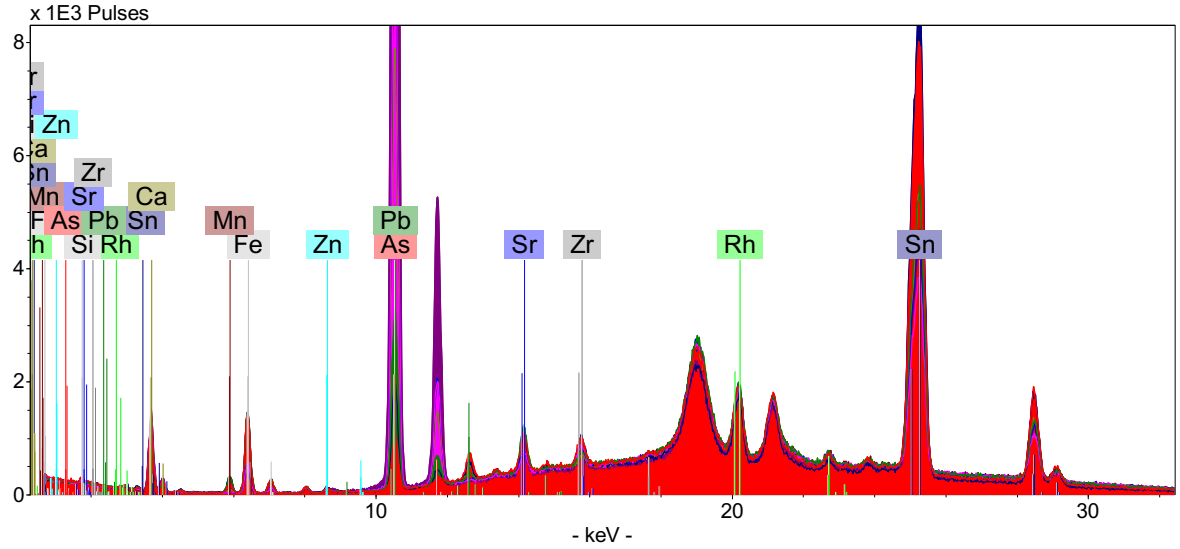


Fig. 14. Handheld XRF spectra of all eight mirrors on the pavilion.

Glass Tank Panes

The ARTAX μXRF was also used to analyze the glass tank panes.[15]

The glass panes of the tank differ in appearance from one another and were likely made by different manufacturing processes. This could suggest replacement of panes over the years. The glass panes with small bubbles and ripples are likely older than the other panes, and may possibly be crown or cylinder glass. The panes without noticeable flaws are likely replacements. Six of the eight panes have flaws and by appearance are possibly older glass. Sides 4 and 8 appear newer.

After analysis, the eight glass tank panes fall into three groupings compositionally, confirming the visual differences. Half of the panes (Sides 2, 3, 5, and 7) have similar spectra containing Ca, Fe, Si, K, Ti, Zr, Sr, and possibly Mn (fig. 15). Panes 4 and 8 have almost the same composition,

[15] X-ray fluorescence has been used to analyze glass for over 50 years (Shugar and Mass 2012, 449). It must be considered that in historic glass the object will be non-uniform, there may be alkali depletion on the surface; quantitative information is really not possible (Shugar and Mass 2012, 451). Colorless glass is mainly light elements. The majority of it is Si, often with Al, and alkali metal oxides and alkaline earth oxides, such as sodium, or potassium oxide. These modifiers stabilize the glass by bridging oxygen atoms. There is usually calcium or magnesium as a stabilizer. There may be lead, zinc, and titanium oxides. Colorants are usually metal oxides or colloidal metals. (Shugar and Mass 2012, 454)

but both contain slightly higher Sr. Panes 1 and 6 contain arsenic, and the spectra are again very similar to each other.

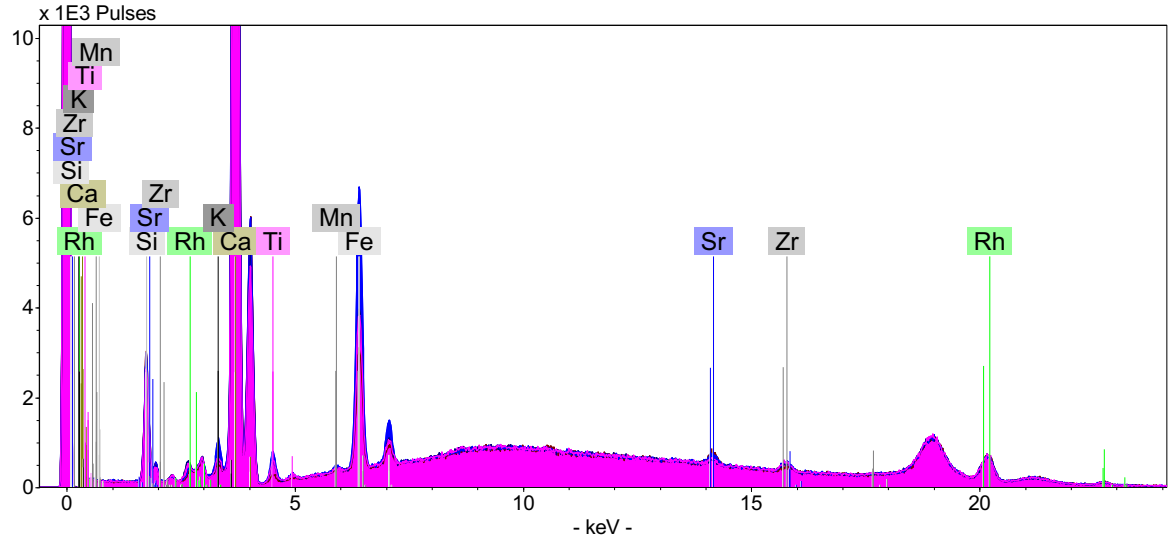


Fig. 15. ARTAX XRF spectra of four of the glass tank panes with similar composition: panes from side 2 (dark red), 3 (pink), 5 (light blue), and 7 (dark blue).

Side 8 seems to be a replacement, as it is broken in the photo sent to Mr. du Pont in the 1940s by the antiques dealer he purchased the aquarium from (fig. 5). Because of the similar elemental composition and similar unflawed visual appearance, it seems likely that Side 4 was replaced around the same time. The half of the panes (Sides 2, 3, 5, and 7) with similar composition are possibly original. Panes 1 and 6, containing arsenic, may be replacements, perhaps earlier than Sides 4 and 8, since they have the flawed appearance of older glass, but it is also possible that they are more recent replacements made to match the older glass. Additionally, it is possible that Sides 1 and 6 are the only original panes in the tank.[16]

[16] As_2O_3 has been used as a refining agent, added to the glass to increase the velocity of bubbles rising to the surface during the refining (bubbles contain gaseous products and trapped air) (Hlavác 1983, 111). The window glass analyzed in the building contains arsenic. Other windows would need to be analyzed to see if they are all of the same composition (only one was analyzed). If the arsenic containing glass panes in the tank are indeed a later addition, this may support the idea that the architectural structure and tank were not originally part of one object. It is also possible that all of the arsenic containing glass is original, and the pieces are all original. Quantitative analysis could possibly be done in the future to more thoroughly characterize the glass and match the levels of elements to historical glass recipes.

Iron Corrosion on the Tank

There are areas with iron corrosion present where tin and paint has been lost (fig. 16). The most textured, orange areas appear to be associated with solder repairs (fig. 16, right).

Fig. 16. Iron corrosion is present where paint and tinning is gone. There are some areas of more textured, more orange corrosion (right), which seem to be associated with solder repairs.

X-ray diffraction[17] was performed on two samples of iron corrosion from the tank. The first sample was from more textured, orange corrosion on the outside of the tank that seems to be associated with solder repairs. Akaganeite (β-FeOOH) was identified as the main component (fig. 17). A sample of more stable-appearing iron corrosion on the inside of the tank framing resulted in various iron oxides, but not akageneite.

[17] X-ray diffraction was carried out using a Rigaku D/max Rapid II diffractometer with a copper anode x-ray tube (45kV, 40mA) and 0.3mm collimator. Powdered material was adhered to the tip of a mounted, non-interfering polymer loop; the mounted sample was then secured to the sample stage. The sample was analyzed in spin mode (0-360° rotation) at a speed of 10°/sec. Rigaku RAPID/XRD software (v.2.4.2) was used for instrument operation and data collection and Rigaku 2DP software (v.2.0.1.1) was used to select the portion of diffraction rings for interpretation. Rigaku PDXL 2 software (v.2.3.1.0) was used to interpret the diffraction pattern, and the Powder Diffraction File from the International Center for Diffraction Data (ICDD) was used as a reference database. Analysis was conducted by Catherine Matsen and interpreted with Catherine Matsen.

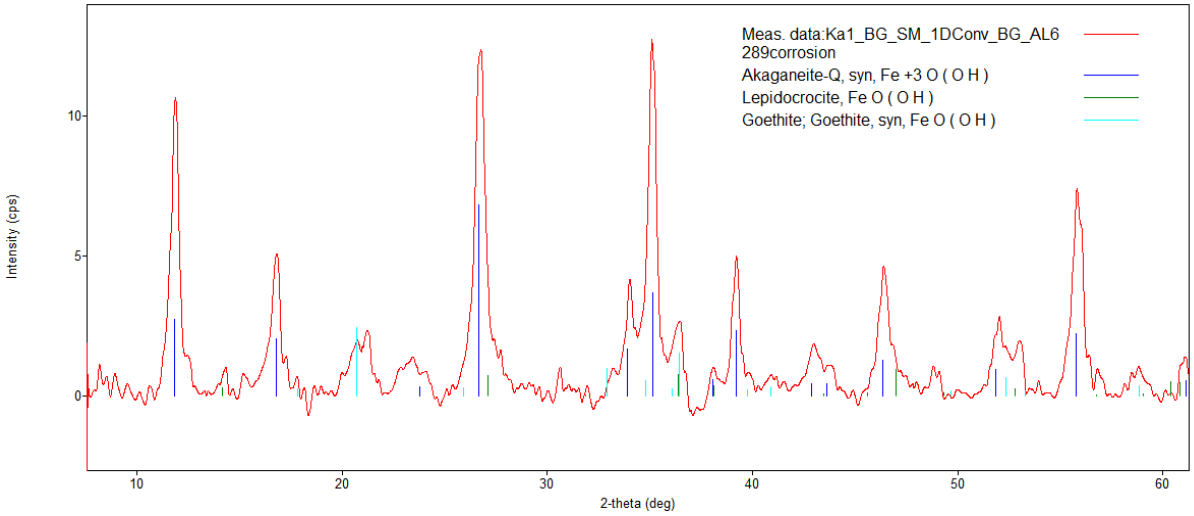


Fig 17. XRD pattern from the orange iron corrosion on the outside of the tank framing, associated with solder repairs. The composition is mainly akaganeite, with other iron corrosion species including lepidocrocite and goethite.

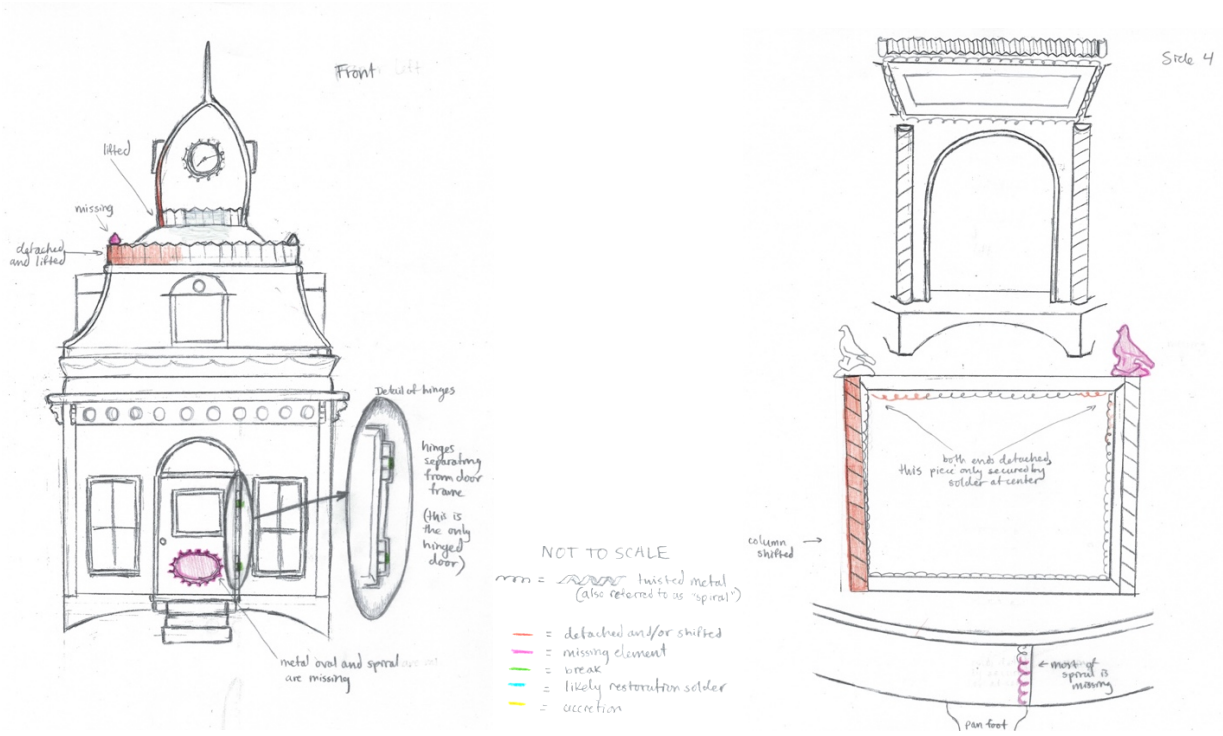
Akaganeite is normally discussed in relation to, and found on, archeological iron or iron in a coastal environment. The presence of akaganeite indicates the presence of chlorides. Akaganeite itself is formed when there is a high concentration of chlorides in an acidic environment and is not itself a threat (Ståhl 2003). However, it can cause corrosion because it has adsorbed chlorides which are mobile in water or high humidity (Watkinson 2017), and it is hygroscopic, attracting water that can then allow the chloride ions to move (Watkinson 2004). Akaganeite may also release chloride ions when it transforms to goethite or hematite (Thickett and Odlyha 2013).

Usual iron corrosion products formed in atmospheric conditions include goethite, lepidocrocite, and magnetite (Watkinson 2017, citing: Hoerlé et al. 2004; Asami and Kikuchi 2003; Morcillo et al. 2011). Lepidocrocite and goethite are among the compounds found on the aquarium. Akageneite was found in an area of worse corrosion, not in the more stable appearing corrosion. Since these areas of more dramatic corrosion are associated with solder repairs, it seems possible that the explanation for the presence of chlorides is that a chloride-containing flux was used for the repairs. It is also possible that chlorine is present in the metallic flake paint (Ferreira et al).[18]

[18] Ferreira et al. studied the bronze powder paint on two 19th century paintings by Swiss artists. The metallic particles and surrounding green agglomerates were analyzed. The authors attributed the presence of chlorine in one and not the other to a difference in preparation of the metallic powder (Ferreira et al. 2015).

DOCUMENTATION AND TREATMENT OF THE OBJECT[19]

Alongside the historical discussion, learning from Rebecca, and carrying out analysis, I was working on the documentation and treating the object. As described above, Rebecca and I agreed on terms for the sections. After this, I diagrammed the sides with numbers, which allowed me to make condition diagrams (fig. 18). Following is a brief summary of some of the treatment steps undertaken.



Figs. 18. I made four of the diagram on the left for the four sides of the building, and eight of the diagram on the right, including corresponding pavilion sides, tank sides, and sections of the pan.

[19] The full "Conservation Treatment Report" is on file at Winterthur.

The components were surfaced cleaned with vacuuming and brushing, and the glass was cleaned on the windows, doors, over the clocks, the tank panes, and the mirrors (fig. 19).

Fig. 19. Cleaning the windows with a small piece of Mr. Clean Streak Free cloth with 1:1 ethanol and deionized water.

The brown scum/corrosion material around the edges of the tank glass was reduced with a combination of mechanical reduction and a citrate solution (0.5% citric acid and 0.5% boric acid in deionized water, adjusted to pH 8.0 with NaOH, with phenoxyethanol) on cotton swabs, which removed the scum without damaging the paint. (This was followed with 1:1 deionized water and ethanol on swabs to clear the solution.)

The corrosion on the tank framing was coated with graphite (figs. 20 and 21). This was chosen after testing corrosion reduction with a scalpel (while effective, it seemed unsafe for this painted tinware) and with an emulsion of an aqueous solution of a chelator in a silicone gel. A graphite stick (6B) was rubbed on the areas of corrosion and the graphite was then spread around with a swab wet with Shellsol D38.

Fig. 20. Area of iron corrosion on the tank before treatment.

Fig. 21. Area of iron corrosion after coating with graphite.

Broken and detached pieces of plastic plant fronds were reattached. Japanese tissue paper was painted with Golden Fluid Acrylics and used to bridge the breaks with Aquazol® 200 in deionized water (figs. 22 and 23). Detached fish fins were also reattached with Aquazol®.

Fig. 22. Attaching the tissue paper to one side of the break.

Fig. 23. Two repairs on the plants (circled).

The grey paint on the architectural structure and the outside of the pan was consolidated using dilute Paraloid® B-48N in xylene with 2-(butylamino)ethanol corrosion inhibitor and precipitated silica matting agent and hydrophobic fumed silica matting agent.

Two replacement pheasants were cast out of Feather Lite™ ultra-lightweight urethane resin, tinted with dry pigments. The casts were shaped with a scalpel and glass paper and tinted with microcrystalline wax with dry pigments.

Detached and bent metal elements were repositioned and reattached with Paraloid® B-48N in xylene with 2-(butylamino)ethanol (fig 24.).

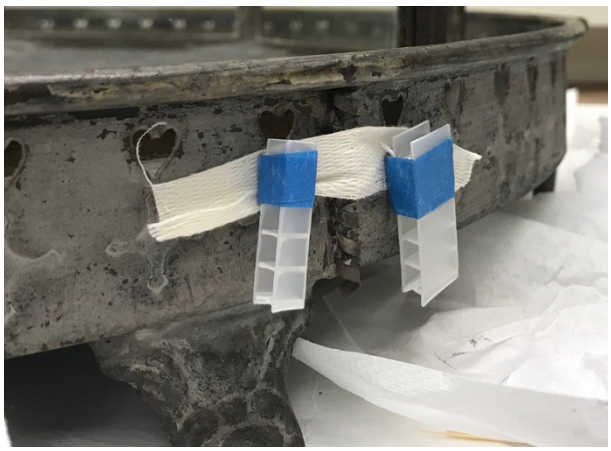


Fig. 24. Holding a reattached spiral in place with twill tape and magnets while the adhesive dried.

Fig. 25. After treatment photograph of the aquarium. Bequest of Henry Francis du Pont 1965.2192

Finally, the components of the aquarium were reassembled (fig. 25). Before reassembly, inscriptions on the inside of the tank were photographed (these seemed to include calculations or measurements and the word "Front"). The architectural structure was placed back in the tank, with the sides offset, after a discussion with curator Ann Wagner.

Treatment of the shattered, faded silk curtains is still needed. This treatment would ideally be connected with further attempts to identify the dye used on the curtains[20], which would potentially allow more solid assumptions on the original color, and then allow discussion of the option of installing reproduction curtains and storing the shattered ones in the dark.

[20] Attempts to identify the dye were made as part of this study, but no results were achieved.

REBECCA DUFFY'S WORK

As I treated the object, Duffy continued with her thesis, which she completed in 2018. She also created a digital exhibit on parlor aquaria. The Winterthur aquarium is one of the objects featured on her website. She created an interactive aspect where the user can hover over different components of the object. She has also been thinking about how to display aquaria more effectively. The effect of an empty tank on a viewer is very different from that of a full aquarium. If the Winterthur aquarium did hold water, the mirrors would have reflected the water and fish. Duffy has wondered if perhaps there is a way to display aquaria using light to provide some effect of water.

CONCLUSIONS

Both of our work benefited from combining our knowledge and our ways of thinking on this project. While we still haven't necessarily solved all of the mysteries of this object, the exchange of Duffy's extensive historical knowledge with the information gained during the technical examination has led to a deeper understanding of this object. We gained information that added to the limited knowledge on the materials of objects like this. This investigation has also raised many new questions.

The collaboration continues: Rebecca Duffy and I gave a joint presentation at a University of Delaware Saturday Symposium at Winterthur in April, a joint presentation at a Winterthur Board Meeting, and we have also discussed the possibility of coauthoring an article.

ACKNOWLEDGMENTS

I am indebted to Rebecca Duffy (WPAMC Fellow, Class of 2019) for her collaboration, enthusiasm, and willingness to share her deep knowledge of 19th century parlor aquaria. I am grateful to Winterthur Objects Conservation advisors Lauren Fair and Lara Kaplan; Winterthur Scientific Research and Analytical Laboratory scientists Dr. Jocelyn Alcántara-García, Dr. Rosie

Grayburn, Catherine Matsen, and Dr. Chris Petersen; curator Ann Wagner; Jim Schneck; and Debbie Hess Norris.

REFERENCES

Alcántara-García, J. 2017. Personal communication. Scientific Research and Analysis Laboratory, Winterthur Museum, Gardens, and Library, Winterthur, Delaware.

Arizio, E., E.F. Orsega, G. Sommariva, and R. Falcone. 2013. Tin amalgam mirrors: investigation by XRF, SEM-EDS, XRD and EPMA-WDS mapping. *Applied Physics A* (111): 733-745.

Bright, L. 2016. Investigations into the Identification of Mercury Mirrors in the Winterthur Collection. Unpublished manuscript, Winterthur Museum, Gardens, and Library, Winterthur, Delaware.

Brunner, B. 2005. *The Ocean at Home: An Illustrated History of the Aquarium*. New York: Princeton Architectural Press.

Cassell, J. C. 1877. *Fair-Hill Terra Cotta Iron Works*. Philadelphia: The Company. Trade Catalog.

de Chavez, K. P. 2010. Historic Mercury Amalgam Mirrors: History, Safety and Preservation. 2010. Technical Bulletin. Williamstown Art Conservation Center Technical Bulletin. Spring 2010. http://www.williamstownart.org/techbulletins/techbulletins.html

Duffy, R. 2017. Parlor Aquaria and Domestic Fishkeeping, 1850-1917. Unpublished manuscript, Winterthur Museum, Gardens, and Library, Winterthur, Delaware.

Duffy, R. 2017. Personal communication. Objects Conservation Lab, Winterthur Museum, Gardens, and Library, Winterthur, Delaware.

Fair, L. 2017. Personal communication. Objects Conservation Lab, Winterthur Museum, Gardens, and Library, Winterthur, Delaware.

Ferreira, E. S. B, D. Gros, K. Wyss, N. C. Scherrer, S. Zumbühl, and F. Marone. 2015. "Faded shine…. The degradation of brass powder in two nineteenth century paintings". *Heritage Science* 3 (1): 1-11.

Gosse, Phillip Henry. 1855. *A Handbook to the Marine Aquarium*. London: John Van Voorst. Available online: https://archive.org/details/ahandbooktomari00gossgoog.

Hamera, Judith. 2011. *Parlor Ponds: The Cultural Work of the American Home Aquarium, 1850-1970.* Ann Arbor, MI: University of Michigan Press.

Hlavǎc, Jan. 1983. *The technology of glass and ceramics: an introduction*. Amsterdam: Elsevier.

Kaplan, L. 2017. Personal communication. Objects Conservation Lab, Winterthur Museum, Gardens, and Library, Winterthur, Delaware.

Matsen, C. 2007. Analytical Report No. 4858. Unpublished manuscript, Winterthur Museum, Gardens, and Library, Winterthur, Delaware.

Matsen, C. 2017. Personal communication. Scientific Research and Analysis Laboratory, Winterthur Museum, Gardens, and Library, Winterthur, Delaware.

Mills, J. and R. White. 1994. *Organic chemistry of museum objects*. Butterworth Heinemann.

Petersen, C. 2017. Personal communication. Scientific Research and Analysis Laboratory, Winterthur Museum, Gardens, and Library, Winterthur, Delaware.

Rohleder, J., F. Tegethoff, F. Wolfgang, and E. Kroker. 2014. *Calcium Carbonate From the Cretaceous Period into the 21st Century*. Birkhauser.

Shugar, A. N., and J. L. Mass. 2012. *Handheld XRF for art and archaeology*. Leuven: Leuven University Press.

Ståhl, K., K. Nielsen, J. Jiang, B.Lebech, J. C. Hanson, P. Norby, J. van Lanschot. 2003. On the akaganéite crystal structure, phase transformations and possible role in post-excavational corrosion of iron artifacts. *Corrosion Scienc*e 45 (11): 2563-2575.

Thickett, D. and M. Odlyha. 2013. The formation and transformation of akaganeite. *Metal 2013 Edinburgh, Scotland: 16th-20th September 2013: interim meeting of the ICOM-CC Metal Working Group, conference proceedings*. 107-113.

Thomas, R. 2015. Dichloromethane Vapour. *ICON news: the magazine of the Institute of Conservation* no. 59 (2015 Jul): 30-32

Veiga, A. R. 2010. Oil painting on tinplate by Francisco José Resende. *Ceroart : Conservation, Exposition, Restauration D'objets D'art.*

Wagner, A. 2017. Personal communication. Objects Conservation Lab, Winterthur Museum, Gardens, and Library, Winterthur, Delaware.

Watkinson, D., and M. Lewis. 2004. The Role of βFeOOH in the Corrosion of Archaeological Iron. *MRS Proceedings* 852.

Watkinson, D. E., N. J. Emmerson. 2017. The impact of aqueous washing on the ability of βFeOOH to corrode iron. *Environmental Science and Pollution Research* 24 (3): 2138–2149.

Winterthur Correspondence File. McKearin 1941-1949. Winterthur Museum, Garden and Library, Winterthur, Delaware.

Winterthur Object Report, Object ID 1965.2192 A, B. EMU Database. Winterthur Museum, Garden and Library, Winterthur, Delaware.

Zumelzu, E., C. Cabezas, and A. Vera. 2006. Scanning Electron Microscopy Analysis of Corrosion Degradation on Tinplate Substrates. *Scanning* 25 (1): 34-36.