

TECHNICAL ANALYSIS OF A BENJAMIN CHANDLEE, JR. TALL CASE CLOCK IN THE WINTERTHUR MUSEUM COLLECTION

LAUREN FAIR

Abstract

A metal clock face constructed by the Philadelphia clockmaker Benjamin Chandlee, Jr., in 1758, and parts of its wooden case are examined using analytical methods in order to determine the materials and degradation products present. The components analyzed are the alloy composition of the metals; fill materials in the recesses of engraved parts on the clock face; paint material on the hands; corrosion product on the metal components; and coating materials and textiles used on the case. The instrumental methods used to conduct this study include energy-dispersive x-ray fluorescence spectroscopy (XRF), scanning electron microscopy with energy-dispersive x-ray microanalysis (SEM-EDS), Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, gas chromatography/mass spectrometry (GC-MS), and polarized light microscopy (PLM). From this analysis, the materials of the clock face were found to be of the period, and remnants of silvering were detected. Most of the metal components on the clock face were identified as copper-zinc alloys, the seconds hand was proven to be blued steel, and a natural resin coating was detected on the spandrel ornaments and hands. Analysis of the finish on the clock case identified early coating materials of pine resin and mineral oil, and the textile fibers on the case were identified as wool and bast fibers. The results of this technical research provide insight into the original design and appearance of the object, which will help determine an appropriate protocol for its treatment.



Fig. 1: Clock face, 2003.032

I. Introduction

This study will reveal the construction materials and methods of manufacture of a 1758 Benjamin Chandlee, Jr. clock face that is part of the Winterthur collection (fig 1). The face, along with its works, is part of a tall case clock that was purchased by Winterthur Museum in 2003 (fig 2). An additional goal of this study is to characterize the coating materials and fragments of textile present on the wooden Chippendale-style case. The clock face and works are currently separated from the case so that the face can undergo conservation treatment. Information gained from this research will help inform the treatment and preservation criteria. In 1991 furniture conservators Mark Anderson and Ridgely Kelly performed treatment on the case, but as yet there have been no technical analyses done on the materials of the clock face, works, or case.

During the eighteenth century, England was considered the center of clock making, and by 1700 the tall case clock had become the most dominant clock form in the home (Distin, 1976). Clockmakers in Colonial America were mostly



Fig. 2: Tall case, 2003.032

following European traditions, but many artisans also forged their own designs and techniques. Clock production was a collaborative effort, however. Mostly it was the clock assembler who would be credited as the maker, but he would order the case from the cabinetmaker, and parts from the brass founder, the wheel and pinion cutter, the bell founder, the silversmith, or the gilder (Arthur, 1967). In early America, the clockmaker would either work with local craftsmen, or parts could be ordered and shipped from England and Europe. Metalworkers were of great demand in Colonial America to provide decorative and utilitarian objects to the early settlers. According to Winterthur Curator emeritus Don Fennimore, “the metals these men (the Colonial braziers, copper and tinsmiths) worked were unquestionably important in the daily lives of Americans during the first century of settlement” (Fennimore, 1975). According to Edwin A. Battison, it was the clockmakers who had the competence and skill in metalwork and mechanical devices that were able to take the lead during the Industrial Revolution and the age of scientific invention (Battison and Kane, 1973).

One such clockmaker and metalworker was Benjamin Chandlee, Jr. He was the grandson of clockmaker Abel Cottey, who is credited as the maker of the first tall case clock in Colonial America in 1709. Abel Cottey received his training in Europe and came to America toward the end of the seventeenth century where he eventually resided in Nottingham, which is present-day Chester County, Pennsylvania. It was in Nottingham that Benjamin Chandlee, Jr., grew up working in the family-owned business *Chandlee & Sons*, and later, *Ellis Chandlee & Brothers*. This particular clock was made in the mid-18th century for Roland Rogers of East Nottingham. Sometime before the year 1816, John Price, who was related to the Chandlee family, acquired the Rogers property along with this clock. It then passed down through the Price family until 1849 when Melicent R. Price married Judge James McCauley of Cecil County, Maryland. Since this date, the clock remained in the McCauley family until the Winterthur Museum purchase in 2003.

Today the tall case clock is appreciated for its design and historical value as well as its nostalgic qualities. Wallace Nutting, a connoisseur of American antiques, writes about tall case clocks in general, “The clock and its case, when both are fine and harmonious, still constitute the most beautiful decoration for an American home” (Nutting, 1933). Since much is known about the history of the Chandlee clock, and it represents an example of early American metalwork and a vital part of American culture, it is important that the analysis and characterization of its materials be conducted so that its aesthetics can be correctly represented and appreciated.

The Chandlee clock face consists of a brass faceplate that is roughly 12 ³/₄” square with an arched top, or lunette, that extends the length five inches. The faceplate is adorned with metal

elements, probably brass, including a large chapter ring that registers the hours and minutes, a seconds ring, cast rococo ornaments located in the spandrels of the lunette, as well as all four corners of the faceplate, and a curved circular nameplate with engraved script that reads “B. Chandlee Nottingham.” These metal elements are attached to the faceplate with a number of pins and/or screws. In the center of the faceplate is a circular stippled field contained by the chapter ring that is decorated with engraving. This central area also contains the seconds ring, the date aperture, and two winding holes used to adjust the time with a gear crank. The clock face has three hands: one each to register the hours, minutes, and seconds. These are made of a ferrous metal, and the minute and hour hands are coated with a black paint. All engraved elements on the main chapter ring, the seconds ring, and the nameplate are filled with a black material.

The movement is attached to the back of the clock face, and it rests on a wooden seatboard. The movement consists of many gears, as well as a striking mechanism, a pendulum, and two lead weights that operate the pulley system. The major components of the movement are most likely brass, while minor parts, including nails, fasteners, rods, etc., are made of a ferrous metal. This study will focus on the characterization of the faceplate components in order to evaluate its aesthetic interpretation.

Early faceplates before 1770 were typically made of brass and measured ten to twelve inches on one side. The chapter rings were also mostly made of brass, and oftentimes they were chemically silvered in order to create a greater contrast with the engraved and filled numbers (Machmer, 1995). Mostly chemical (electro-plating) methods were employed to silver clock dials of this period. One source from 1902 lists many recipes for silvering that vary upon the brightness or quality desired: some of the combinations include using a paste of silver nitrate and cream of tartar, cyanide of silver and carbonate of ammonia, or adding bisulphide of carbon to either of these mixtures to ensure a brighter silver surface (Philip, 1902). Analysis performed during this study may elucidate if a silvering process was used, and if so, which one. It is not clear, given visual examination alone, whether the chapter ring of the Chandlee clock was silvered at one time or not. A silver layer from any silvering process would result in an extremely thin layer, thus making it susceptible to damage from polishing. This might explain the lack of silver on the surface presently. The detection of silver on the surface using XRF would strongly suggest that the chapter ring was originally silvered.

Exposed areas of the faceplate, as well as the chapter ring and the engraved nameplate in the lunette, exhibit a reddish corrosion product that is finely distributed over the surface of the metal. Elemental analysis of the metals will determine if they are indeed brass. Brass is composed of

copper alloyed with zinc, and sometimes traces of other elements like lead or tin. The brasses can be divided into three categories based on the type of phase present: alpha brasses with up to 35% zinc; alpha + beta brasses with 35-46.6% zinc; and beta brasses with 46.6-50.6% zinc (Scott, 1991). Most historic brasses are alpha brasses. Those made prior to 1738 (when zinc became economically available as a free metal in Europe) were made by a cementation process, whereby sheets of copper were stacked with zinc carbonate and heated so that the zinc would diffuse into the copper; this process yielded brasses with up to 28% zinc, the upper limit for this process (Rivers and Umney, 2003). These different alloy compositions greatly affect the physical properties of the brass. For example, increased zinc contents (above 15 wt.%) make the alloy more susceptible to a process known as “dezincification,” where the zinc is leached from the brass, and the yellow color of the copper-zinc alloy changes to a pink color of the residual copper (Selwyn, 2004). Copper-zinc alloys can undergo dezincification when exposed to certain environmental conditions, acidic cleaning solutions, or ammonia containing polishes (Anderson, 2008). If certain products were used to clean or polish the brass on the faceplate and chapter ring, the reddish color now observed on the surface could be due to dezincification. In one section of a 1977 book on watches and clocks entitled “Workshop Hints and Helps,” the author suggests the use of nitric acid mixed with sulfuric acid or potassium nitrate to clean brass elements on clocks (de Carle, 1977). The analysis of this study will characterize the corrosion product present on the clock face.

The cast ornaments that adorn the spandrels in the lunette and the four corners of the faceplate will also be analyzed to determine their metal alloy compositions. Historically, these cast ornaments were either brass or pewter, and they were often ordered from England and shipped to America (Arthur, 1967). A small segment of one of the corner ornaments is broken from the main piece, but both are still attached to the faceplate via small pins. In addition to elemental analysis, this small separated piece will be dismantled and analyzed using SEM secondary electron imaging in order to characterize the surface morphology of the ornaments and elucidate the methods of manufacture.

Historical documents and texts state that clockmakers would often fill the engraved numbers and lines of the chapter rings and nameplates with a “hard black wax” (Machmer, 1995). Another source suggests that a paste made of “shellac, methylated spirit and lamp-black” can be rubbed into the engravings of a clock dial (de Carle, 1977). The black fill material in the recesses of the engraved elements on the Winterthur clock face will be analyzed for characterization.

The hands are all made of a ferrous metal, as they exhibit magnetism, and elemental analysis will be conducted to confirm this. On most early American clock faces, the hands were made of finely

wrought blued steel. The seconds hand has a surface appearance that may be due to remnants of a bluing process. Given the stylistic difference of each hand in relation to one another, it is of interest to know whether the hands are of the same alloy composition, or if they are different. The minute and hour hands are also coated with a black paint. Small samples of this coating will be analyzed to determine the medium, and the seconds hand will be analyzed to determine if it is indeed blued steel. Results of these analyses may or may not support that all of the hands are original.

Although there does not exist much in the literature in the way of scientific studies on clock faces, in 2007 Winterthur/University of Delaware graduates Debra Breslin and Samantha Springer performed conservation treatment on a John Turnbull clock face and movement that belonged to Beauvoir Museum in Louisiana (Breslin, 2007; Springer, 2007). As part of their documentation and conservation treatment report, XRF was performed on the metal components of the faceplate, hands, and parts of the works; FTIR was carried out on green corrosion products in the numerals, the fill material in the engraved numerals, and the coating on the reverse of the faceplate; finally, GC-MS was used to look at the green corrosion product as well as the resinous materials in the engraved numerals. The results of the XRF analysis found the brass plate to be a copper alloy with 35-40% zinc, with trace amounts of iron and lead, the components of the clock movement were found to be brass with approximately 25% zinc content, and the hands (which included a black coating) were determined to be mostly iron with trace amounts of copper, zinc, lead, calcium, and titanium. The results of the FTIR found the black fill material of the engraved numerals to consist of a pine resin and calcite. The FTIR and GC-MS analysis of the corrosion products was inconclusive.

Another Winterthur/University of Delaware student project, performed by Catherine Coueignoux, employed analytical equipment to study Winterthur Museum's Peter Stretch clock, 2004.51 (Coueignoux, 2006). Ultraviolet light examination, XRF, FTIR, GC-MS, and Raman spectroscopy were performed on the clock face. XRF identified the metal faceplate components as copper-zinc alloys, with the chapter ring, second dial, and nameplate all having a layer of silvering. The hands were identified with XRF to be ferrous, and one was determined to be a replacement. Analysis of coatings present on the clock face using FTIR and GC-MS found that a restoration coating of cellulose nitrate was applied to replace a previous coating of oil and pine resin. Turmeric may also have been identified from samples taken from the spandrels as a tinting agent in the natural resin coating.

Metallographic examinations have been employed to reveal the grain structures of metals, to yield information on manufacture techniques; metallography is performed by taking a cross-section from the metal object, polishing and etching the mounted sample, and examining it under a microscope (Rivers and Umney, 2003). Killian Anheuser has studied fire-gilding and electro-plating techniques by metallographic study as well as gilding replication experiments (Anheuser, 1997). Instrumental analytical methods used to characterize metal alloys include XRF, SEM-EDS, atomic absorption spectroscopy (AA), neutron activation (NA), emission spectroscopy (ES), proton induced x-ray/gamma-ray emission (PIXE/PIGE), and photon activation; methods used to characterize corrosion products include x-ray diffraction and infrared absorption spectroscopy (Rivers and Umney, 2003).

Winterthur Museum Analytical Laboratory's Janice Carlson conducted a study on twenty-eight brass candlesticks from the 15th-18th centuries from England and/or France. Carlson used XRF to determine metal alloy compositions in order to better characterize the objects and possibly determine their provenance (Carlson, 1999). Quantitative energy-dispersive x-ray fluorescence analysis was employed using a Kevex EXACT program calibrated with Winterthur's brass standard 29.8. Alloy compositions of twenty-seven of the candlesticks were found to be 83.0-68.3% copper, 2.3-25.7% zinc, 0.3-4.8% tin, and 0.2-10.5% lead; while one of the candlesticks (England, 1550-1600) showed 14.8% lead and 7.42% tin.

Various studies on the use of analytical methods to detect gilding and characterize gilding processes on metals were published in Drayman-Weisser's book, *Gilded Metals* (2000). One article by Susanne Gänsicke and Richard Newman from the Museum of Fine Arts, Boston, is a study of gilded silver from ancient Nubia (Gänsicke and Newman, 2000). They discuss the use of microscopic and metallographic techniques to analyze cross sections, as well as the quantitative analysis with XRF on objects that could not be sampled. Their results identified the use of two types of gilding processes: diffusion bonding and mercury gilding.

The analysis of two gilded bronze sculptures from the Athenian Agora discussed in another article published in Drayman-Weisser's book (Paterakis, 2000). Both bronzes were gilded with sheets of silver using diffusion bonding and the foil gilding method, and only traces of the original gilded silver remain. The bronzes were analyzed in the 1970s using atomic absorption spectroscopy (AAS) and SEM. The author calls for further study using optical metallography and the SEM with microprobe to determine the morphology of the gold as applied to the silver, the technique used for diffusion bonding, and the method of securing the gilded silver sheets. Another study included in

Drayman-Weisser's publication discusses the uses of SEM-EDS to determine gilding methods and to characterize the surface morphology of metal samples (Centeno and Schorsch, 2000). Finally, one article tests the use of XRF to detect the presence of mercury when the process of mercury gilding is suspected, and this technique was found to be successful (Lins and Malenka, 2000).

As mentioned earlier, a second part of this study will be to analyze the coating materials and fragments of textile on the clock case. Although the case was treated in 1991 and the finish at that time was cleaned and papered with 320 wet grit paper in order to reduce severe alligatoring of the surface, some areas of the underlying coatings were not disturbed (Anderson and Kelly, 1991). At the time of the 1991 treatment, the sanded parts were treated with Cellusolve, and a new coating of a 10% solution of dammar resin in xylene was applied, in addition to BriBrown wax and dabbing of shellac mixed with Orasol dyes in some areas. Analysis of the

coatings aims to identify and characterize original coating materials. A few fragments of textile, which are presumed to be original to the construction of the case, still remain within the hood (fig 3).

Oftentimes, silk was the material used to cover the insides of the decorative carvings on the sides of the case hood (Anderson, 2008). These fibers will be sampled to perform fiber identification using polarized light microscopy.



Fig. 3: View inside top hood of Chandlee clock case

Coueignoux's technical study of Winterthur's Peter Stretch clock of 1735 also focused on the analysis of coatings present on the tall mahogany case. Cross section microscopy, XRF, FTIR, GC-MS, and SEM-EDS were used to identify the complex coating history observed on the case and determine the original coating materials. On samples believed to contain a full coating history, analysis showed at least four generations of coatings with natural resins (identified as pine resin or copal) and polish/dirt layers of oil and wax (identified as beeswax) in between the second, third, and fourth generations.

The furniture coatings on a 1785 mahogany rolltop desk attributed to David Roentgen in the Decorative Arts collection of the J. Paul Getty Museum were examined using transmission FTIR spectroscopy (Derrick, Stulik, and Landry, 1999). The aim of the study was to characterize the coating, to determine whether the case had been refinished and if the original finish remained. Samples were taken, embedded in polyester resin, and thinly sectioned with a glass knife. This thin section was placed on a BaF₂ window for photodocumentation followed by IR analysis. This method was chosen to characterize each layer in the section. Through this method, they were able

to determine the bottom layers contained shellac, a layer on top of this that contained calcium carbonate (perhaps used to polish the underlying shellac layer), and analysis of the top clear layer showed that it consisted of a mixture of shellac and cellulose nitrate.

Instruments used for analysis of the Chandlee clock face and case were chosen based on their appropriateness in analyzing the materials present, as well as on the extent possible to sample. The information gained from this study will greatly inform the aesthetic treatment of this object. The value and importance of the clock in the Winterthur collection warrants a careful examination and characterization of the materials in order to ensure its correct interpretation.

II. Experimental Procedures

A variety of analytical techniques were necessary to characterize the materials of the clock face as well as the multiple layers of coatings and fragments of textile on the wooden case. All samples were small (no more than a few micrograms or fibers) and taken from discreet areas on the object. The procedures and instrumentation used in this study are outlined in the order in which they were performed.

Energy Dispersive X-Ray Fluorescence (XRF):

An ArtTAX μ XRF spectrometer with a molybdenum tube and Si detector was employed for qualitative and semi-quantitative elemental analysis of all metal components of the clock face. XRF analysis provided alloy composition data for all the major metal components. This instrument has an approximately 70-100 micron spot size, and operates at a 600 μ A current, with a tube voltage of 50 kV, and collection times averaging around 100 seconds. A collection time of 300 seconds was employed when silver was detected on certain parts of the clock face to obtain a better signal-to-noise ratio. The instrument can detect low-energy elements as low as potassium ($Z \geq 19$) and as high as uranium ($Z=92$) in open-air usage. For this type of analysis, no sample or sample preparation is necessary. Intax version 4.5.18.1 software was used to gather and interpret the spectra.

This spectroscopic technique measures the characteristic x-rays emitted by a particular element, a phenomenon that occurs when atoms of that element are struck with incident x-rays, causing inner shell electrons to be ejected from the atom and higher energy electrons to fall and fill vacancies in lower levels. The fluorescence is detected by a detector and converted to an interpretable spectrum, making possible the identification of major and minor elements present, based on their x-ray energies, as well as their relative concentrations.

Energy Dispersive Scanning Electron Microscopy with X-ray Microanalysis (SEM-EDS):

Samples of corrosion products were examined using SEM-EDS to gain elemental and compositional data. Samples were mounted directly onto a carbon stub with SPI supplied double-sided carbon tape adhesive. Samples and objects were examined using a Topcon ABT-60 scanning electron microscope with an accelerating voltage of 20 kV, at working distances of 25.5 and 37.5 mm, 390X magnification, and a sample tilt of 20°. The EDS data was analyzed with the Bruker X-flash detector and microanalysis Quantax model 200 with Esprit 1.8 software. Back-scattered electron (BSE) images, energy-dispersive spectroscopy (EDS) spectra, and elemental maps were gathered for all samples.

SEM-EDS allows for elemental analysis, as well as topographical information of the samples with secondary electron imaging. Back-scattered electron imaging and X-ray mapping can create an elemental map of the sample surface to help understand changes in the composition of the artifact.

Fourier Transform Infrared Spectroscopy (FTIR):

Samples of corrosion products on the clock face, black fill material in the engraved numerals, black paint on the hands, and coating materials on the case were taken and prepared for qualitative analysis with FTIR. Samples were prepared, under a Nikon SMZ800 stereo-binocular microscope and a Sony Trinitron monitor, and rolled flat with a steel roller onto a diamond half-cell. An area was left clear on each cell in order to use this area to subtract from the background. A Nicolet 6700 FT-IR Spectrometer with a mercury-cadmium-telluride detector, equipped with a (Thermo)Nicolet Continuum FT-IR Microscope in transmission mode was employed. This instrument operates in the spectral range of 4000-650 cm^{-1} at a spectral resolution of 4 cm^{-1} and a collection of 128 scans. The OMNIC software (version 8) allows for baseline correction and access to IRUG, Aldrich, Gettens, and Hummel spectral libraries.

In transmission FTIR, incident IR radiation passes through a sample and is absorbed by the sample, causing changes in vibrational and rotational energy levels in atoms of certain molecules. These absorptions, or absorption bands, occur at certain frequencies that are characteristic for a particular molecule or class of molecules. This generates spectra of peaks composed of these characteristic absorption bands, and they can be associated with a class of compounds through the identification of major functional groups present. The region in which many of these associations can be drawn is called the fingerprint region (1500-500 cm^{-1}). Interpretation is done by a trained eye and with a good spectral library as a source; often mixtures and impurities of the sample make data extraction difficult and challenging.

Dispersive Raman Microanalysis (Raman):

Raman is a complimentary technique to FTIR. Samples were placed on a microscope slide, except for the analysis of surface treatment of the seconds hand, which was small enough to fit below the microscope objective, eliminating the need for a sample. A Renishaw inVia Dispersive Raman Microscope with either a 514nm or 785nm laser scanning for was the source used for qualitative analysis of the samples. The laser operates in the 3200-100 cm^{-1} spectral range with a resolution of 3 cm^{-1} and a scan time of 20 seconds at varying powers from 0-10% with the 785nm laser and 10-50% with the 514nm laser. The generated spectra was interpreted with Galactic Grams and OMNIC software and compared to reference spectra available. The spectroscopic reference, *The Renishaw Raman database of gemological and mineralogical materials* (Williams, et. al, 1997), was also consulted.

Raman spectroscopy operates by detecting molecular vibrations that occur due to electromagnetic wave scattering when a sample is irradiated with a wavelength-specific (from the visible to the near IR) laser beam. The scattered radiation detectable by the Raman CCD detector is mostly due to its symmetrical vibrations, which are responsible for changes in polarizability within the molecule. The Raman phenomenon occurs when molecules are excited to an electronic state and fall back down to a ground state at a different energy level. These energy differences are measured and converted to yield spectra that are unique to each compound.

Gas Chromatography-Mass Spectrometry (GC-MS):

GC-MS was useful in analyzing coating and fill materials present on the clock face as well as the coating materials on the case. A Hewlett Packard HP 6890 series gas chromatography system with a HP5973 mass selective detector and a 7883 automatic liquid injector was used for gas chromatographic separation and mass spectrometric analysis. This method was helpful to complement and supplement results obtained from FTIR analysis. GC-MS can identify compounds based on retention time and mass spectrum for each component. In GC, the components of a sample are separated by their affinity to the stationary phase or the mobile phase. Due to the accurate reproducibility of GC, it is possible to identify components by comparing retention times to a library of reference standards. The samples are ionized in a vacuum accelerated in an electric field, separated based on the m/z ratio, and then detected by an electron multiplier.

Each sample was placed in a capped heavy-walled vial (100-300 μL) and $\sim 100\mu\text{L}$ of 1:2 MethPrep II reagent (Alltech) in benzene was added, and the vial was warmed at 60°C for one hour. The sample was used directly for injection into the GC-MS with an inlet and transfer line

temperature at 300°C. The injection hardware cleans itself and injects the sample automatically to ensure even and consistent sample size. Analysis was carried out using the RTLMPREP method on the GC-MS.

Polarizing Light Microscopy (PLM):

A few tiny fibers were sampled with the aid of optivisors from the pieces of textile located on the interior of the clock case hood. The fibers were placed on a microscope slide in a few drops of de-ionized water and teased out under a stereo-binocular microscope using insect pins. PLM was carried out using a Nikon Eclipse E600 polarizing light microscope with a 10X ocular and 10X, 20X, and 40X objectives. The microscope is attached to a computer monitor and equipped with a Nikon RTKE digital camera for image capture. Images were viewed and processed using Nikon Act-1 software (version 2.63). Fiber identification was carried out with the aid of a McCrone reference set of known fiber samples as well as consulting literature sources on the identification of textile fibers. PLM allows for the identification of fibers by their characteristic visual qualities at the microscopic level.

III. Results

Tables 1 through 7 below show the results from instrumental analysis for the different parts of the clock face (fig 4), as well as the case. All sample locations are documented in additional diagrams found in the Appendix. Additional data from analysis is also located in the Appendix.

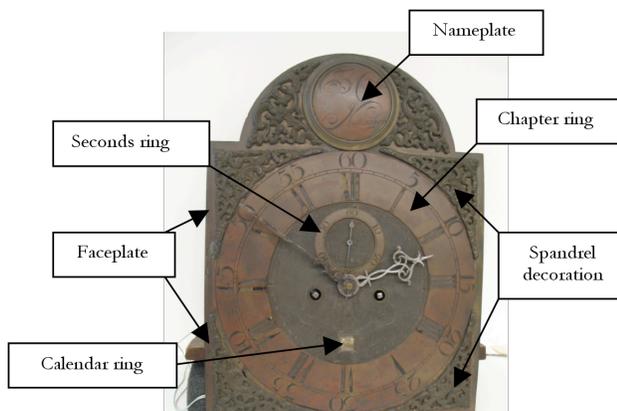


Fig. 4: Chandlee clock face, 2003.0032

Table 1. Summary of analysis from faceplate

Sample number	Sample description	Analytical instrument	Results
5217_A, B	Faceplate	XRF	Major: Cu, Zn Minor: Fe, Pb
5217_1	Green/white corrosion product in an isolated area on the faceplate	SEM-EDS	Cu, Zn, S, Fe, Ca, K, Cl, Si, Al, Mg, O
		Raman	Ettringite $(\text{CaO})_6(\text{Al}_2\text{O}_3)(\text{SO}_3)_3 \cdot 32 \text{H}_2\text{O}$ or Polyhalite $(\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2(\text{H}_2\text{O}))$
		FTIR	Sulfate
5217_2, 3, 4	Coating on faceplate	FTIR	Iron oxide, plant resin
		GC-MS	Carnauba wax
5217_5	Coating verso faceplate	FTIR	Bitumen, zinc stearate

Table 2. Summary of analysis from central stippled field

Sample number	Sample description	Analytical instrument	Results
5217_C, D	Central stippled field	XRF	Major: Cu, Zn Minor: Fe, Pb
5217_6	Brown, red, green corrosion product even all over surface	SEM-EDS	Cu, Zn, Fe, Ti, Ca, K, Cl, S, P, Si, Al, O, Mg

Table 3. Summary of analysis from chapter ring, seconds ring, and calendar ring

Sample number	Sample description	Analytical instrument	Results
5217_E, F, G, H	Chapter ring	XRF	Major: Cu, Zn Minor: Fe, Pb
5217_I, J	Seconds ring	XRF	Major: Cu, Zn Minor: Fe, Pb
AL5217_7, 8, 9	Fill material in engraved numerals of chapter ring and seconds ring	FTIR	Beeswax, plant resin
		GC-MS	Beeswax, pine resin
AL5217_K, L, M	Calendar ring	XRF	Major: Cu, Zn Trace: Ag
AL5217_10	Coating on calendar ring	FTIR	Zinc stearate, sodium polyacrylate, gypsum
		GC-MS	Pine resin

Table 4. Summary of analysis from nameplate

Sample number	Sample description	Analytical instrument	Results
5217_N	Nameplate, recto	XRF	Major: Cu, Zn Minor: Fe, Pb
5217_O, P	Nameplate, verso	XRF	Major: Cu, Zn Minor: Fe, Pb, Ni
5217_Q, R	Nameplate ring	XRF	Major: Cu, Zn Minor: Fe, Pb
5217_11	Corrosion product outside edge nameplate	SEM-EDS	Cu, Zn, Fe, Ca, K, Ag, Cl, S, P, Mg, O, Al, Si

Table 5. Summary of analysis from spandrel ornaments

Sample number	Sample description	Analytical instrument	Results
5217_S, T, U, V, W, X	Spandrel ornaments	XRF	Major: Cu, Zn Minor: Fe, Pb, Ni
5217_12	Coating upper proper right spandrel	GC-MS	Pine resin, drying oil
5217_13	Coating upper proper left spandrel	FTIR	Plant resin
5217_14	Coating lower proper right spandrel	FTIR	Gum, gypsum, malachite
		Raman	Azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$)
		GC-MS	Pine resin, drying oil

Table 6. Summary of analysis from hands

Sample number	Sample description	Analytical instrument	Results
5217_Y	Hour hand, recto	XRF	Major: Fe Minor: Cu, Zn
5217_Z	Hour hand, verso	XRF	Major: Fe Minor: Cu, Zn, Ca
5217_AA	Minute hand, recto	XRF	Major: Fe Minor: Cu, Zn, Ca
5217_BB	Minute hand, verso	XRF	Major: Fe Minor: N/A
5217_CC	Seconds hand, recto	XRF	Major: Fe Minor: Mn
		Raman	Magnetite (Fe_3O_4)
5217_15, 16	Paint on hour and minute hands	FTIR	Mineral oil, verdigris
		GC-MS	Pine resin, drying oil

Table 7. Summary of analysis from case

Sample number	Sample description	Analytical instrument	Results
Case_1	Coating proper right front side by foot	GC-MS	Mineral wax
Case_2	Coating inner lip of door	FTIR	Beeswax
		GC-MS	Mineral wax, beeswax
Case_3	Coating of blanché area beneath proper left rosette on hood	GC-MS	Pine resin, drying oil, mineral wax
Case_4	Coating of replacement piece: proper left rosette on hood	GC-MS	Shellac
Case_5	Coating proper left fretwork of hood	GC-MS	Pine resin, mineral wax
Fiber_1	Tan warps and yellow wefts from back of soundboard	PLM	Tan warps are wool; yellow wefts are a bast fiber
Fiber-2	Tan warps and wefts from spandrel fretwork in hood	PLM	Bast fibers

Clock face:

From XRF analysis, it was determined the faceplate, central stippled field, chapter ring, seconds ring, calendar ring, nameplate, nameplate ring, and spandrels all have copper and zinc as the major elements. The calendar ring has evidence of the presence of silver, present in the form of silvering on a copper-zinc alloy substrate (fig 5).

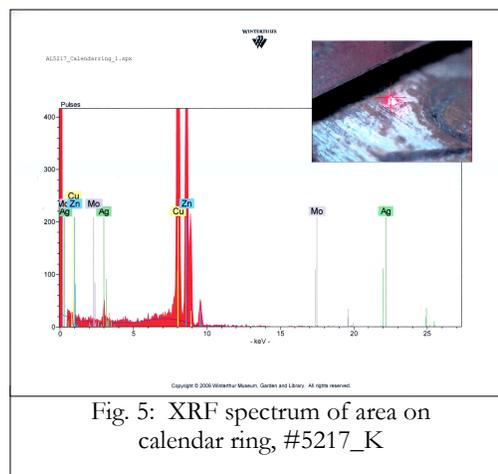
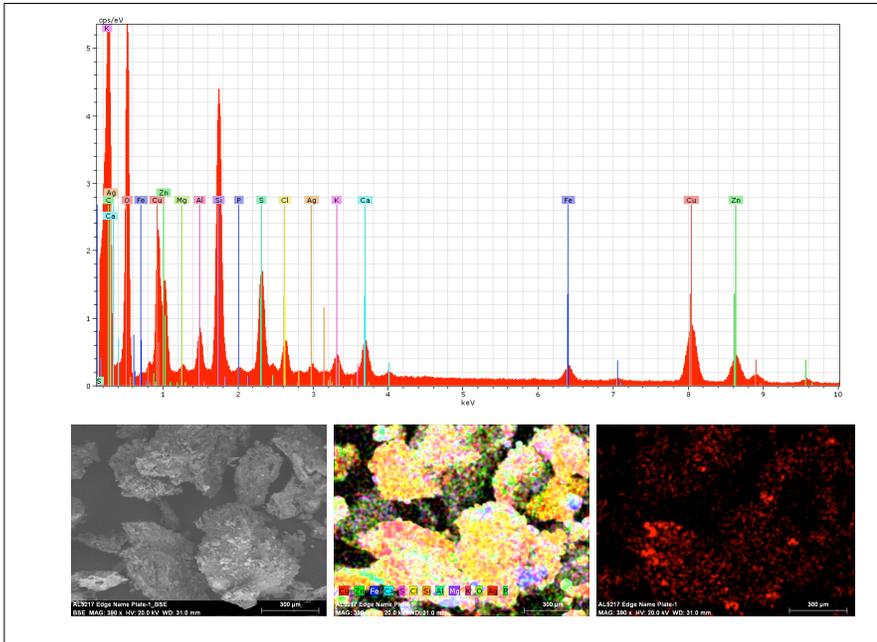


Fig. 5: XRF spectrum of area on calendar ring, #5217_K



No evidence of silver was found with XRF on any of the other components suspected of having been silvered at one time (i.e. the chapter ring, seconds ring, and nameplate). Silver was found, however, using SEM-EDS to analyze sample #5217_11, an area of corrosion product from the outside edge of the nameplate (fig 6).

Fig. 6: SEM-EDS spectrum (top) for #5217_11, showing presence of Ag; back-scattered image of sample (left); elemental map (center); and map of Ag (right)

Sample #5217_1, the green/white corrosion product in an isolated area of the

faceplate, was analyzed using SEM-EDS, Raman spectroscopy and FTIR (figs 7, 8, 9, 10). From the combined results of these three techniques, the green corrosion product on the proper right side of the faceplate is likely ettringite $((CaO)_6(Al_2O_3)(SO_3)_3 \cdot 32 H_2O)$, or polyhalite $(K_2Ca_2Mg(SO_4)_4 \cdot 2(H_2O))$.

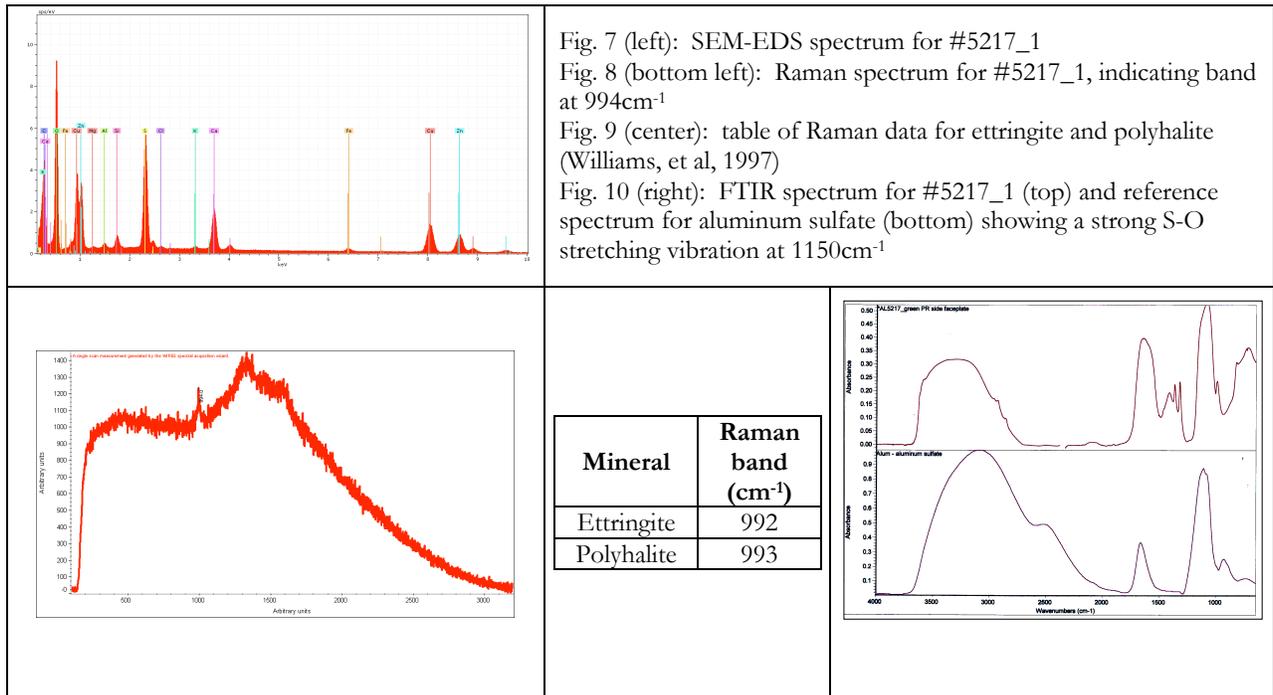
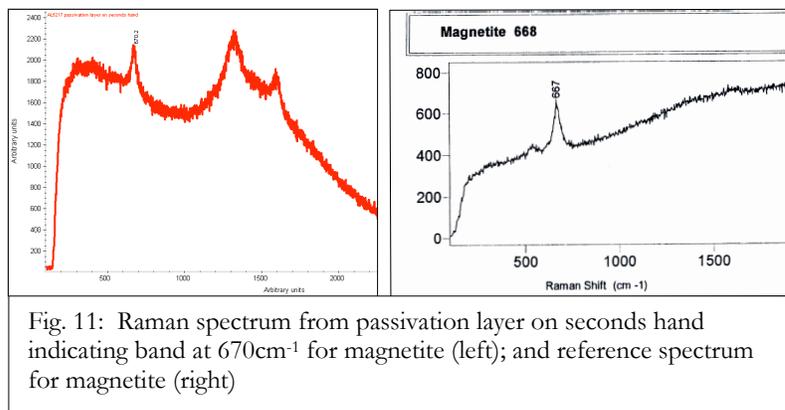


Fig. 7 (left): SEM-EDS spectrum for #5217_1
 Fig. 8 (bottom left): Raman spectrum for #5217_1, indicating band at 994cm⁻¹
 Fig. 9 (center): table of Raman data for ettringite and polyhalite (Williams, et al, 1997)
 Fig. 10 (right): FTIR spectrum for #5217_1 (top) and reference spectrum for aluminum sulfate (bottom) showing a strong S-O stretching vibration at 1150cm⁻¹

All three hands were found to be ferrous with trace elements of copper and zinc where there is no paint and the additional trace element of calcium where paint is present. The paint on both the hour and minute hands was found to contain pine resin and a drying



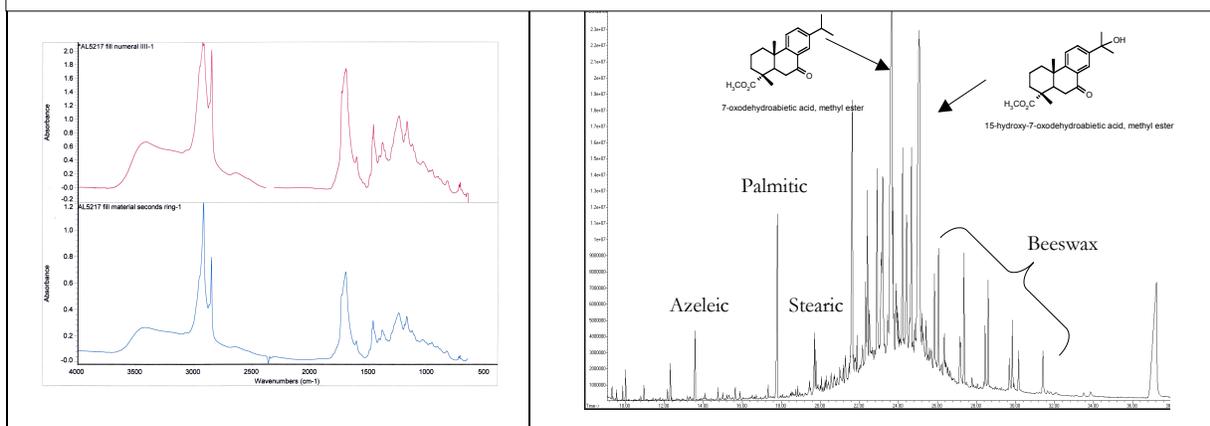
oil, confirmed by GC-MS. Raman spectroscopy also identified the presence of magnetite (Fe₃O₄) on the seconds hand, confirming this hand is blued (fig 11).

In addition to the pine resin/drying oil coating present on the hour and minute hands, this same coating was found on all samples taken from the spandrel decoration. In some coating samples from the spandrel ornaments, azurite (Cu₃(CO₃)₂(OH)₂ identified by Raman) and malachite (identified by FTIR) were also found. Analysis of coatings on the calendar ring with FTIR revealed a complex mixture of materials, and only a small amount of pine resin could be identified with GC-MS.

A sample from the black coating on the verso of the faceplate was identified as bitumen with FTIR. On the recto of the faceplate, carnauba wax was identified with GC-MS from samples that were extracted from cotton swabs using n-methyl-2-pyrrolidinone solvent.

The fill material in the engraved numerals is the same on both the chapter ring and seconds ring and was found to be a mixture of pine resin and beeswax, confirmed by FTIR and GC-MS (figs 12, 13). Raman analysis of the black fill material was inconclusive, since the bands for carbon in the Raman spectrum could not be distinguished between a black pigmenting agent and the presence of carbon from the laser charring the sample.

Fig. 12 (left): FTIR spectra for #5217_7(top) and #5217_9(bottom) showing the fill material of the chapter ring and seconds ring are the same
Fig. 13 (right): GC-MS chromatogram for #5217_7 showing presence of pine resin (abietic acid methyl esters), beeswax (long chain hydrocarbons), and a drying oil (methyl esters of palmitic, stearic, and azelaic acids)



Clock case:

GC-MS was the most useful technique to analyze the coatings present on the clock case, although no stratigraphic information was gained. Coating samples taken from areas expected to have original material in addition to restoration coatings were found to contain pine resin, a drying oil, an abundance of mineral oil, and in some cases, beeswax (fig 14). Sample #case_4 taken from a later replacement piece on the hood was identified as shellac with GC-MS.

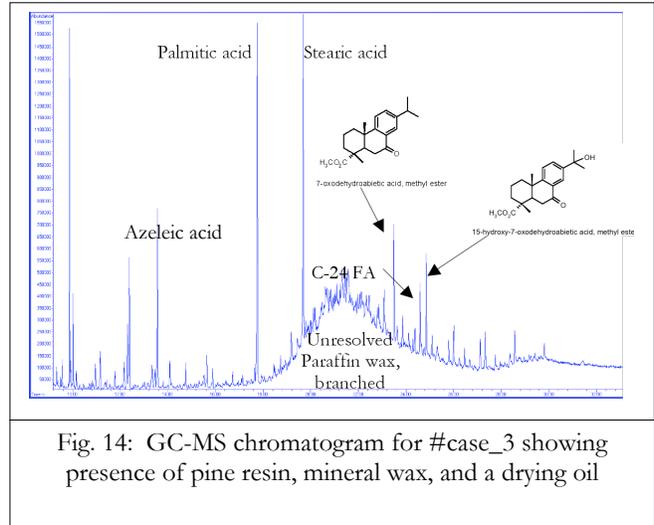


Fig. 14: GC-MS chromatogram for #case_3 showing presence of pine resin, mineral wax, and a drying oil

Using polarized light microscopy, the fibers on the back of the soundboard were identified as wool and bast fibers, as seen in the comparison of the photomicrograms of #fiber_1 to McCrone reference samples (figs 15, 16). The fibers present inside the fretwork on the case hood were identified as bast fibers.

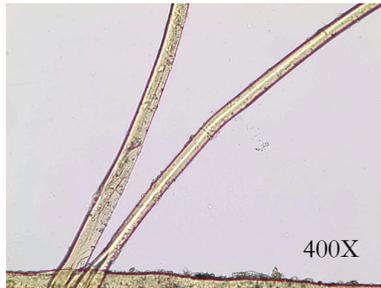
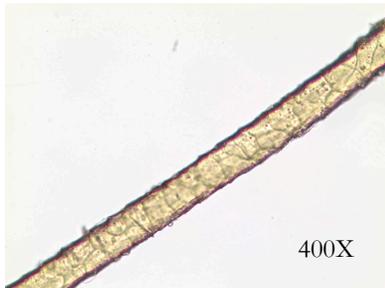


Fig 15: #fiber_1 tan warp (left); and yellow weft (right)

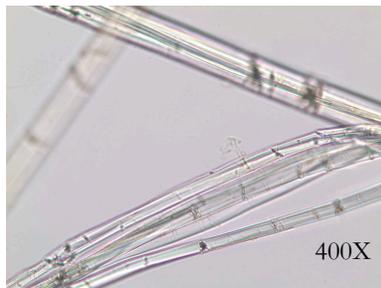
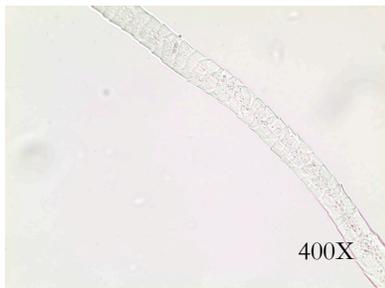


Fig 16: McCrone merino wool reference (left); and McCrone flax reference (right)

IV. Discussion

The results from this technical study have identified the majority of materials present on the clock face and case. For the most part, the findings are congruent with what is known in the art historical literature about tall case clock manufacture in the eighteenth century. The findings also offer insight into the original aesthetic of the clock face, as well as its current condition.

Clock face:

Identification of copper and zinc as the metal alloy components of the faceplate, chapter ring, seconds ring, calendar ring, nameplate, and central field corroborates the 1758 creation date of the clock face, as manufacture materials for clock faces of this time period were mostly brass. The spandrels were also identified as a copper-zinc alloys, confirming that they were cast from brass, not pewter. Precise quantitative analysis of the metal alloys was not carried out as a part of this technical study. In the future, the XRF data obtained in this research could be used for quantitative analysis to determine copper-zinc ratios of the metal clock parts by comparing them to a brass reference. In addition, the broken segment of the upper proper right spandrel could not be analyzed with SEM secondary electron imaging because this segment was attached to the faceplate with solder and could not be removed.

The detection of silver on the outside edge of the name plate as well as on the calendar ring suggests that the chapter ring, seconds ring, and nameplate were all originally silvered, and the calendar ring retains its silvered surface. XRF did not detect the presence of mercury in any location, suggesting the technique of mercury gilding was not employed. The silvering process used cannot be determined at this time, since taking cross-section samples of the metal was not permitted for this study, eliminating the possibility of performing further analysis with SEM or metallographic techniques. If samples of metal could be taken for analytical purposes in the future, the technique used to silver the chapter ring, seconds ring, nameplate and calendar ring might be discovered.

Examination of the blackened corrosion product present on the central stippled field of the clock face exposed an abundance of alumino-silicates as well as iron and magnesium, and the SEM showed that the corrosion is evenly distributed across the surface. This indicates a finely-distributed layer of dirt and/or polish residue on the central plate. The isolated area of green/white corrosion was found to be a calcium-alumino-sulfate material, either ettringite or polyhalite. This may be due to polishing residue left behind from a previous polishing campaign. Iron oxide polish residues were also detected with FTIR on samples taken from the surface of the faceplate. Given the

detection of polish residues on the clock face, it can be suggested that parts of the clock face were polished and/or cleaned with chemicals that could alter the surface appearance of the metal. Therefore, it is not surprising that the more exposed areas on the face are reddish in appearance and that no silver remains on the once-silvered areas.

The fill material in the engraved numerals of both the chapter ring and seconds ring was identified as a pine resin and beeswax mixture, as confirmed by GC-MS, and this is congruent with the description in the literature of the black fill material as a “hard black wax.” Raman was an unsuccessful technique in identifying the pigmenting agent.

All three hands on the clock face have been found to contain iron, with trace amounts of copper and zinc. This was expected based on the frequent use of steel for manufacturing clock hands in the eighteenth century. It was also common to create a passivation layer of magnetite on the surface of the steel hands, adding further protection from corrosion. Magnetite was identified on the surface of the seconds hand with Raman, indicating this hand was created using traditional methods. The non-blued hour and minute hands are both painted black on one side, and this paint was found to contain oils as well as calcium, the latter of which could be indicative of the pigmenting agent, as in bone black, which contains calcium phosphate (Gettens and Stout, 1942). Raman was again unsuccessful in identifying the black pigment.

A sample of the coating on the hour hand was compared to coating samples from two of the spandrel ornaments. Pine resin and a drying oil was identified in all three samples, as confirmed with GC-MS data, suggesting that the same coating applied to the spandrel ornaments was also applied over the black paint on the minute and hour hands. Pine resin was also identified with GC-MS as an original coating on the brass spandrel ornaments of Winterthur’s 1735 Peter Stretch clock (Coueignoux, 2006). One sample taken from the coating on a spandrel ornament was found to contain azurite with Raman, while another was found to contain malachite with FTIR; these are believed to be copper corrosion products now imbedded in the spandrel coatings.

In addition to the coatings found on the hands and spandrel ornaments, coatings were also identified on the faceplate and calendar ring. The entire verso of the faceplate was found to be coated with bitumen with FTIR. Bitumen is a black petroleum-derived substance that was often used to coat the verso of clock faceplates in order to protect them from corrosion (Pouliot, 2008). Carnauba wax was identified on the recto of the faceplate with GC-MS. This material was uncovered after some corrosion removal from the surface of the faceplate; it is believed this wax could have been applied in the past and is now imbedded and covered over with corrosion (Pouliot,

Wolbers, 2009). Coatings on the calendar ring were not able to be fully identified. Samples analyzed showed a complex mixture of materials, the only clear component recognizable was a small amount of pine resin.

Clock case:

From analysis of the coatings on the clock case, it was hoped to elucidate original coating materials left in tact from the 1991 conservation treatment. Cross section microscopy was not performed because the later coating materials were known. Therefore, samples were taken from inconspicuous areas where early coating material was believed to remain, and these were analyzed with GC-MS in comparison with a sample taken from a known replacement piece that did not have any original coatings. Pine resin, a drying oil, mineral wax, and a small amount of beeswax were found in areas believed to contain early coatings, while the sample from the replacement piece was found to be shellac. Since it was known that conservation materials applied in the 1991 treatment included dammar resin, Briwax (mixture of beeswax and carnauba wax), shellac and orasol dyes, at least two early materials can be suggested: pine resin and mineral wax. Mineral waxes are fractions from the distillation of petroleum and are different from plant wax and beeswax because they tend to be purer, in the sense that they do not contain many of the alcohols or esters present in the latter materials (Mills and White, 2003). Pine resin is a period coating present on many pieces of furniture from the eighteenth century, including clock cases (Coueignoux, 2006).

The question of whether the textile fibers present on the hood of the clock case are silk has also been answered. The textile on the back of the soundboard was identified as a wool-and-bast fiber blend, while the textile beneath the fretwork on the front of the hood was found to contain only bast fibers. Linen, one of the most common of the bast fibers, was being frequently used in the American colonies for the production textiles for many different uses, and it was often sold in a blend with wool known as “linsey-woolsey” (Merrimack Valley Textile Museum, 1980). While silk needed to be imported from China, both linen and wool were more readily-available in America, and may explain the use of these fibers on the Benjamin Chandlee, Jr. clock case.

V. Conclusion

With many of the questions about construction materials of the 1758 Benjamin Chandlee, Jr. tall case clock now answered, a more appropriate aesthetic can be interpreted. The clock face is comprised of metal alloys, coatings, and fill materials that are all of the period. The identification of

silver through technical analysis proves that the current appearance of the clock face is far from what it was originally. The current lack of silver and reddish appearance of some of the copper-alloys are explained by previous polishing/cleaning campaigns. An earlier finish on the case has been identified, distinguishing it from later coatings applied in the 1991 conservation treatment. The textile fibers present on the case hood have also been identified.

The decision for different conservation treatment approaches for the clock face will be based largely in part on the results of this scientific investigation. The darkened corroded surfaces of the faceplate, central stippled plate, and spandrel ornaments will be reduced and/or polished to bring back the intended brassy color. The chapter ring, seconds ring, and nameplate will be treated with a coating of silver paint or gilded with leaf to yield the intended appearance of a silvered-brass surface. Material characterization through this study will also inform inherent solubilities and vulnerabilities of the organic constituents so that chosen conservation materials can be completely reversible and distinguishable from original materials. It is hoped that with information gleaned from this study, the clock face can receive treatment that will return it to its original aesthetic appearance.

VI. Acknowledgements

I would like to thank the following people for their support and guidance throughout this project. This academic research could not have been accomplished without the assistance and dedication of the scientists in Winterthur's Scientific Research and Analytical Laboratory, particularly Dr. Jennifer Mass, Dr. Joseph Weber, Catherine Matsen, and Dr. Chris Petersen. I would also like to thank my classmate Jessica Arista who is jointly involved with the conservation treatment of the clock face. I thank Winterthur curators Ann Wagner and Wendy Cooper for their involvement and enthusiasm in the many discussions about this clock. The collaboration between conservators of many disciplines has been an invaluable contribution to this study, and could not have been completed without them: namely, major supervisor Bruno Pouliot for his continued support and treatment expertise; conservation scientist Richard Wolbers for his constant investment in characterizing corrosion products and treatment methods; furniture conservator Mark Anderson for his supervision and advice regarding the clock case as well as construction methods of the clock face; textile conservator Joy Gardiner for her expertise on the textile components of the case; and paintings conservators Mary McGinn and Joyce Hill Stoner for their knowledge of coatings and gilding methods. Special thanks goes to Terry Drayman-Weisser from the Walters Art Museum for her input regarding clock faces and her particular expertise in metals, and to gilded objects conservators William Lewin and Davida Kovner for their valued advice regarding gilding methods. Finally, I would like to thank all of my classmates from the WUDPAC class of 2010 for their never-ending support and friendship.

VII. References

- Anderson, M. 2008. Personal communication. Conservation department, Winterthur Museum.
- Anderson, M., and R. Kelly. 1991. Wood Object Conservation Report for Chandlee Clock, L89.1310, Winterthur Museum.
- Anheuser, K. 1997. The practice and characterization of historic fire gilding techniques. In *JOM Journal of the Minerals, Metals and Materials Society*. Boston: Springer. Vol. 49, No. 11, 58-62.
- Battison, E. A., and P. E. Kane. 1973. *The American Clock: 1725-1865: The Mabel Brady Garvan and Other Collections at Yale University*. Greenwich, Connecticut: The New York Graphic Society Limited.
- Breslin, D. 2007. Object conservation report for Turnball clock dial plate and hands, 2006R-999-3035 B (ACP 1234), Winterthur Museum.
- Carlson, J. H. 1999. Analytical report: The Winterthur Museum Analytical Library. In *The English Candlestick: 1425-1925*. London: Christie's Books Limited. 244-252.
- Centeno, S. A., and D. Schorsch. 2000. The Characterisation of Gold Layers on Copper Artifacts from the Piura Valley (Peru) in the Early Intermediate Period. In *Gilded Metals: History, Technology and Conservation*. London: Archetype Publications in association with The American Institute for Conservation of Historic and Artistic Works. 223-240.
- Coueignoux, C. 2006. "The Scientific Analysis of Winterthur's Peter Stretch Clock: a Characterization of Materials and Construction History and Implications for the Object." Winterthur Museum.
- de Carle, D. 1977. *Watch & Clock Encyclopedia*. New York: Bonanza Books by arrangement with Norwood Publications (N.A.G. Press).
- Derrick, M. R., D. Stulik, and J. M. Landry. 1999. *Infrared Spectroscopy in Conservation Science: Scientific Tools for Conservation*. The Getty Conservation Institute: The J. Paul Getty Trust.
- Distin, W. H., and R. Bishop. 1976. *The American Clock*. New York: E.P. Dutton & Co., Inc.
- Fennimore, D. L. 1975. Metalwork. In *American Art Journal* Vol. 7, No. 1: 93-106.
- Gänsicke, S., and R. Newman. 2000. Gilded Silver from Ancient Nubia. In *Gilded Metals: History, Technology and Conservation*. Ed. Terry Drayman-Weisser. Archetype Publications in association with The American Institute for Conservation of Historic and Artistic Works. 73-96.
- Gettens, R. J. and G. L. Stout. 1942. *Painting Materials: A Short Encyclopedia*. New York: Dover Publications, Inc.

- Lins, A., and S. Malenka. 2000. The Use of Mercury Salts in Gold Electroplating. In *Gilded Metals: History, Technology and Conservation*. London: Archetype Publications in association with The American Institute for Conservation of Historic and Artistic Works. 267-282.
- Machmer, R. S., and Rosemarie B. 1995. *Berks County Tall-Case Clocks, 1750 to 1850*. Reading, PA: The Historical Society Press of Berks County, Pennsylvania.
- Merrimack Valley Textile Museum. 1980. *All Sorts of Good Sufficient Cloth: Linen-Making in New England, 1640-1860*. North Andover, Massachusetts.
- Mills, J. S., and R. White. 2003. *The Organic Chemistry of Museum Objects*, 2nd ed. New York: Butterworth-Heinemann.
- Nutting, W. *Furniture Treasury*. Vol. III. 1933. New York: MacMillan Publishing Co., Inc.
- Paterakis, A. B. 2000. Two Gilded Bronze Sculptures from the Athenian Agora. In *Gilded Metals: History, Technology and Conservation*. Ed. Terry Drayman-Weisser. Archetype Publications in association with The American Institute for Conservation of Historic and Artistic Works. 97-107.
- Philip, Arnold. 1902. *The Electro-Plating and Electro-Refining of Metals*. New York: D. Van Nostrand Company.
- Pouliot, B. P. 2008. Personal Communication. Art Conservation Department, Winterthur Museum, Winterthur, Delaware.
- Rivers, S., and N. Umney. 2003. *Conservation of Furniture*. New York: Elsevier Butterworth-Heinemann.
- Scott, D. A. 1991. *Metallography and Microstructure of Ancient and Historic Metals*. The J. Paul Getty Museum: The Getty Conservation Institute, in association with Archetype Books.
- Selwyn, L. 2004. *Metals and Corrosion: A Handbook for the Conservation Professional*. Canada: Canadian Conservation Institute.
- Springer, S. 2007. Object conservation report for Turnbull clock movement and seat board, minus pendulum and weights, 2006R-999-3035 B (ACP 1234b), Winterthur Museum.
- Wagner, Ann. 2008. Personal communication. Curatorial Department, Winterthur Museum, Winterthur, Delaware.
- Williams, K. P. J, J. Nelson, and S. Dyer. 1997. *The Renishaw Raman database of gemological and mineralogical materials*. Renishaw Precision Metrology and Inspection Equipment.
- Wolbers, R. 2009. Personal communication. Conservation Department, Winterthur Museum, Winterthur, Delaware.

Bibliography

- Anderson, M. 2008. Personal communication. Conservation department, Winterthur Museum, Winterthur, Delaware.
- Anderson, M., and R. Kelly. 1991. Wood Object Conservation Report for Chandlee Clock, L89.1310, Winterthur Museum.
- Anheuser, K. 1997. The practice and characterization of historic fire gilding techniques. In *JOM Journal of the Minerals, Metals and Materials Society*. Boston: Springer. Vol. 49, No. 11, 58-62.
- Atil, E., W. T. Chase, and P. Jett. 1985. *Islamic Metalwork*. Washington, D.C.: The Smithsonian Institution.
- Battison, E. A., and P. E. Kane. 1973. *The American Clock: 1725-1865: The Mabel Brady Garvan and Other Collections at Yale University*. Greenwich, Connecticut: The New York Graphic Society Limited.
- Breslin, D. 2007. Object conservation report for Turnball clock dial plate and hands, 2006R-999-3035 B (ACP 1234), Winterthur Museum.
- Carlson, J. H. 1999. Analytical report: The Winterthur Museum Analytical Library. In *The English Candlestick: 1425-1925*. London: Christie's Books Limited. 244-252.
- Centeno, S. A., and D. Schorsch. 2000. The Characterisation of Gold Layers on Copper Artifacts from the Piura Valley (Peru) in the Early Intermediate Period. In *Gilded Metals: History, Technology and Conservation*. London: Archetype Publications in association with The American Institute for Conservation of Historic and Artistic Works. 223-240.
- Chandlee, E. E. 1943. *Six Quaker Clockmakers*. Philadelphia: The Historical Society of Pennsylvania.
- Coueignoux, C. 2006. "The Scientific Analysis of Winterthur's Peter Stretch Clock: a Characterization of Materials and Construction History and Implications for the Object." Winterthur Museum.
- de Carle, D. 1977. *Watch & Clock Encyclopedia*. New York: Bonanza Books by arrangement with Norwood Publications (N.A.G. Press).
- Derrick, M. R., D. Stulik, and J. M. Landry. 1999. *Infrared Spectroscopy in Conservation Science: Scientific Tools for Conservation*. The Getty Conservation Institute: The J. Paul Getty Trust.
- Drayman-Weisser, T. 2000. *Gilded Metals: History, Technology and Conservation*. London: Archetype Publications in association with The American Institute for Conservation of Historic and Artistic Works.
- Eckhardt, G. H. 1955. *Pennsylvania Clocks and Clockmakers*. New York: The Devin-Adair Company.
- Fennimore, D. L. 1975. Metalwork. In *American Art Journal* Vol. 7, No. 1: 93-106.

- Gänsicke, S., and R. Newman. 2000. Gilded Silver from Ancient Nubia. In *Gilded Metals: History, Technology and Conservation*. Ed. Terry Drayman-Weisser. Archetype Publications in association with The American Institute for Conservation of Historic and Artistic Works. 73-96.
- Gettens, R. J. and G. L. Stout. 1942. *Painting Materials: A Short Encyclopedia*. New York: Dover Publications, Inc.
- Greaves, P. H., and B. P. Saville. 1995. *Microscopy of Textile Fibers*. Great Britain: Biddles Ltd.
- James, A. E. 1947 and 1967. *Chester County Clocks and Their Makers*. Exton, PA: Schiffer Publishing, Ltd.
- Lins, A., and S. Malenka. 2000. The Use of Mercury Salts in Gold Electroplating. In *Gilded Metals: History, Technology and Conservation*. London: Archetype Publications in association with The American Institute for Conservation of Historic and Artistic Works. 267-282.
- Machmer, R. S., and Rosemarie B. 1995. *Berks County Tall-Case Clocks, 1750 to 1850*. Reading, PA: The Historical Society Press of Berks County, Pennsylvania.
- Martinón-Torres, M., R. V. Rojas, J. Cooper, and T. Rehren. 2007. Metals, microanalysis and meaning: a study of metal objects excavated from the indigenous cemetery of El Chorro de Maíta, Cuba. In *Journal of Archaeological Science* 34: 194-204.
- Mass, J. 2008. Personal communication. Conservation department, Winterthur Museum, Winterthur, Delaware.
- Mayer, D. 2007. Notes from Fiber Identification Workshop. Winterthur/University of Delaware Program in Art Conservation.
- Merrimack Valley Textile Museum. 1980. *All Sorts of Good Sufficient Cloth: Linen-Making in New England, 1640-1860*. North Andover, Massachusetts.
- Mills, J. S., and R. White. 2003. *The Organic Chemistry of Museum Objects*, 2nd ed. New York: Butterworth-Heinemann.
- Nutting, W. *Furniture Treasury*. Vol. III. 1933. New York: MacMillan Publishing Co., Inc.
- Paterakis, A. B. 2000. Two Gilded Bronze Sculptures from the Athenian Agora. In *Gilded Metals: History, Technology and Conservation*. Ed. Terry Drayman-Weisser. Archetype Publications in association with The American Institute for Conservation of Historic and Artistic Works. 97-107.
- Philip, Arnold. 1902. *The Electro-Plating and Electro-Refining of Metals*. New York: D. Van Nostrand Company.

- Pouliot, B. P. 2008. Personal Communication. Art Conservation Department, Winterthur Museum, Winterthur, Delaware.
- Rivers, S., and N. Umney. 2003. *Conservation of Furniture*. New York: Elsevier Butterworth-Heinemann.
- Scott, D. A. 1991. *Metallography and Microstructure of Ancient and Historic Metals*. The J. Paul Getty Museum: The Getty Conservation Institute, in association with Archetype Books.
- Springer, S. 2007. Object conservation report for Turnbull clock movement and seat board, minus pendulum and weights, 2006R-999-3035 B (ACP 1234b), Winterthur Museum.
- The Textile Institute. 1975. *Identification of Textile Materials*. London: Manara Printing Services.
- Wagner, Ann. 2008. Personal communication. Curatorial Department, Winterthur Museum, Winterthur, Delaware.
- Wildman, A. B. 1954. *The Microscopy of Animal Textile Fibers*. London: Lund Humphries.
- Williams, K. P. J, J. Nelson, and S. Dyer. 1997. *The Renishaw Raman database of gemological and mineralogical materials*. Renishaw Precision Metrology and Inspection Equipment.
- Wolbers, R. 2009. Personal communication. Conservation Department, Winterthur Museum, Winterthur, Delaware.

Appendix

- A. Diagrams of clock face and case showing all locations of sampling
- B. XRF spectra
- C. SEM-EDS spectra, back-scattered images, and elemental maps
- D. FTIR spectra
- E. Raman spectra
- F. GC-MS chromatograms and select ion spectrometry
- G. Photomicrograms from fiber analysis with PLM

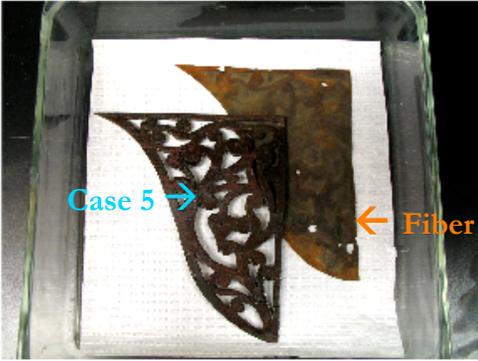
Appendix A: Diagram of clock face showing all locations analyzed with XRF



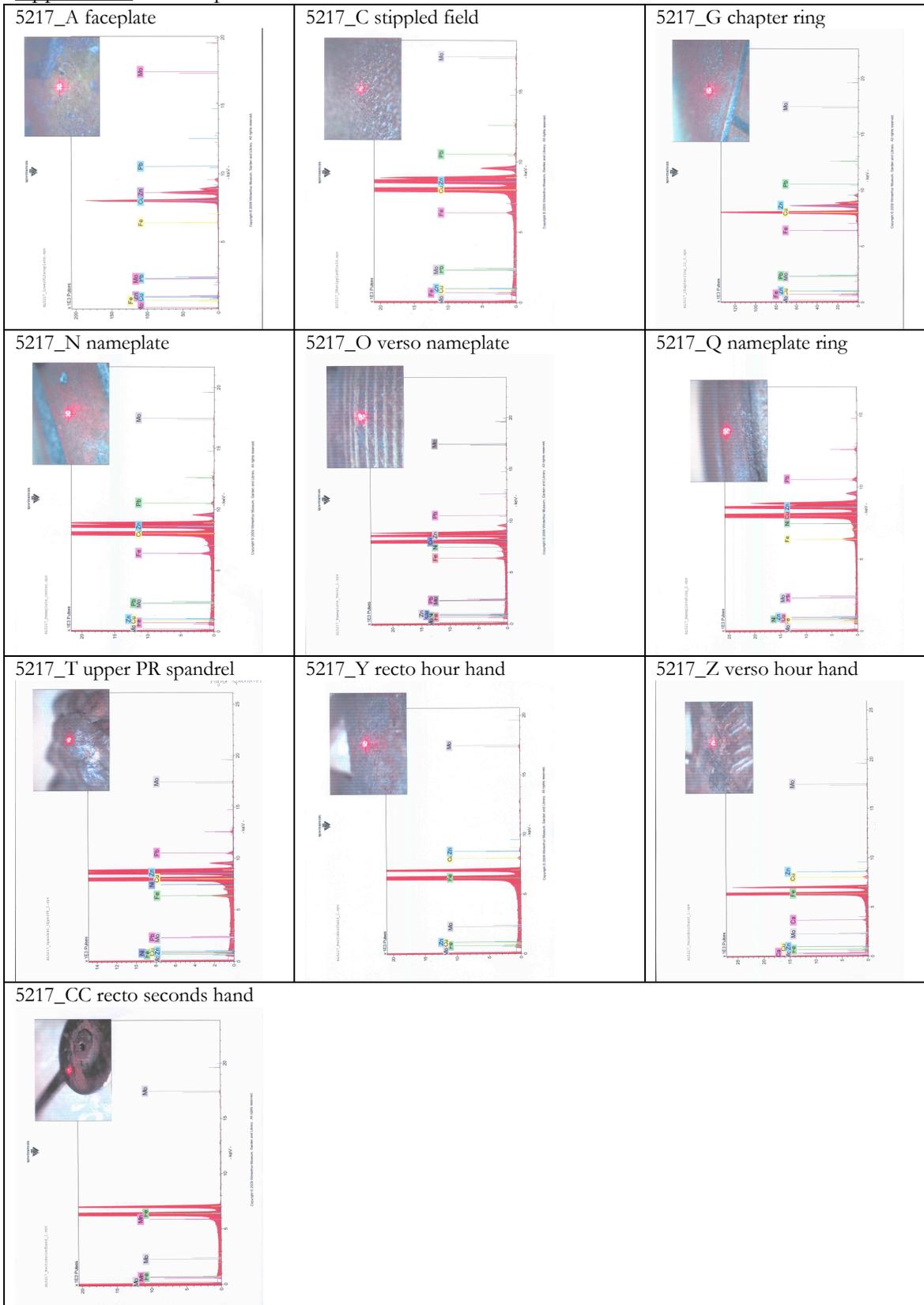
Appendix A: Diagram of clock face showing all locations of samples



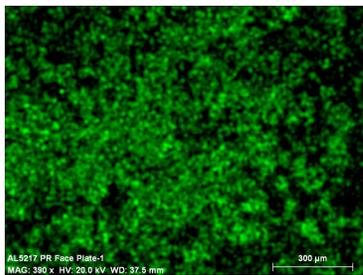
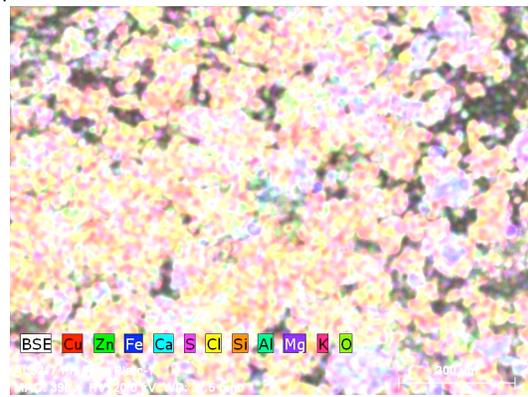
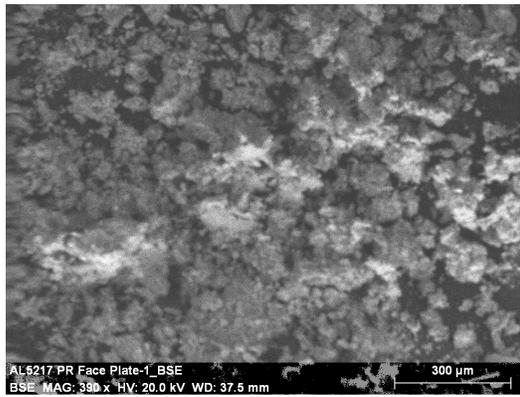
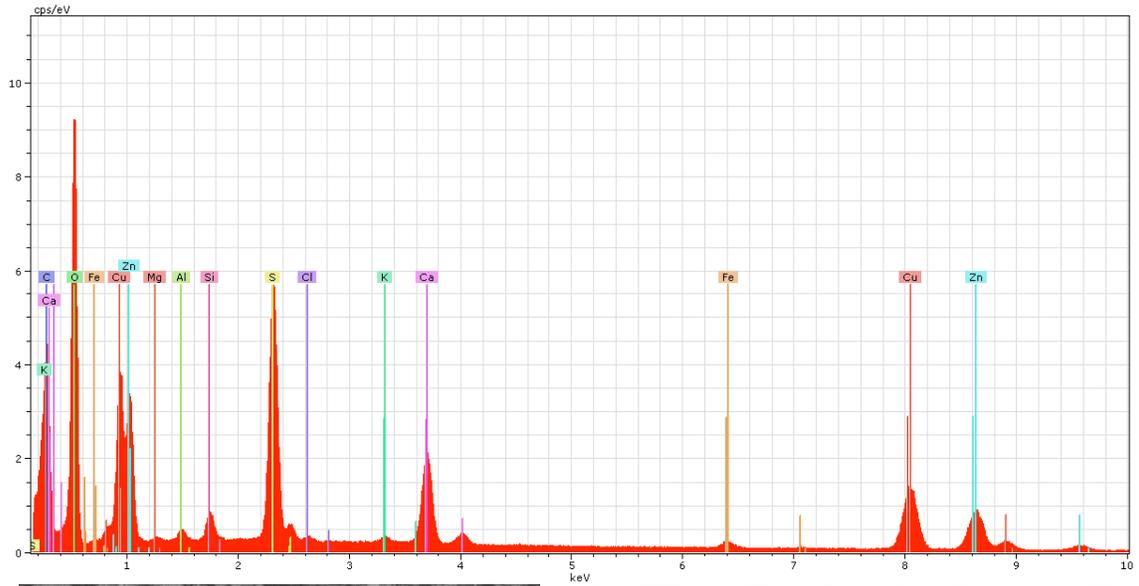
Appendix A: Diagram of parts of case showing all locations of samples



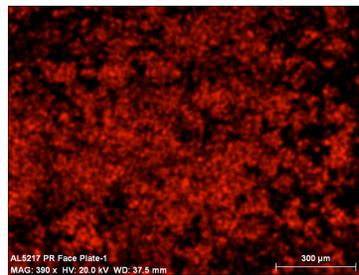
Appendix B: XRF spectra



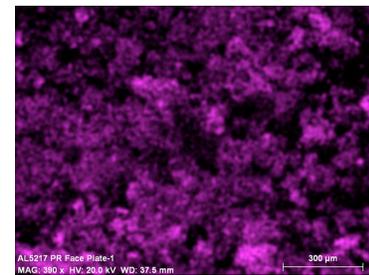
Appendix C: SEM-EDS data
5217_1 green corrosion product proper right side faceplate



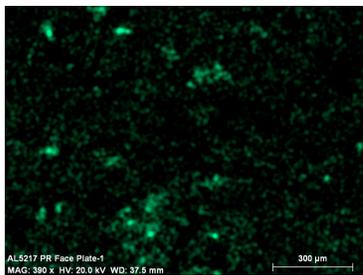
Zinc



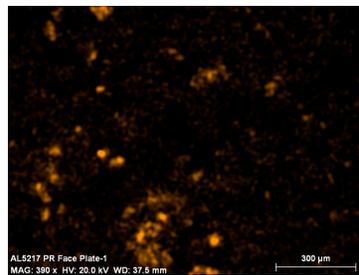
Copper



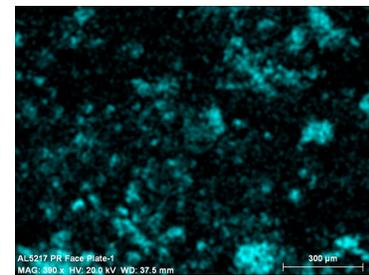
Sulfur



Aluminum

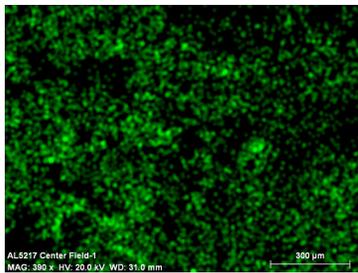
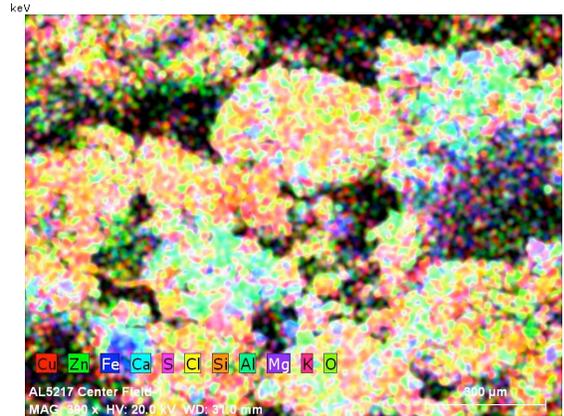
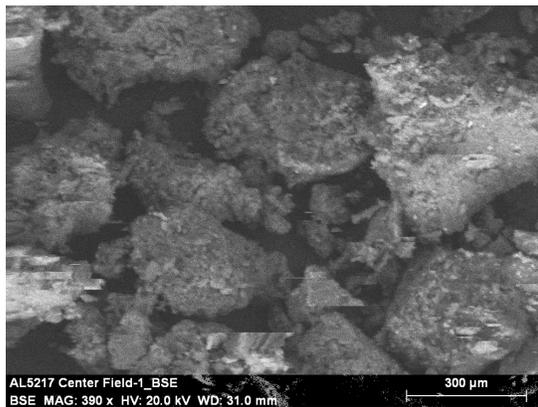
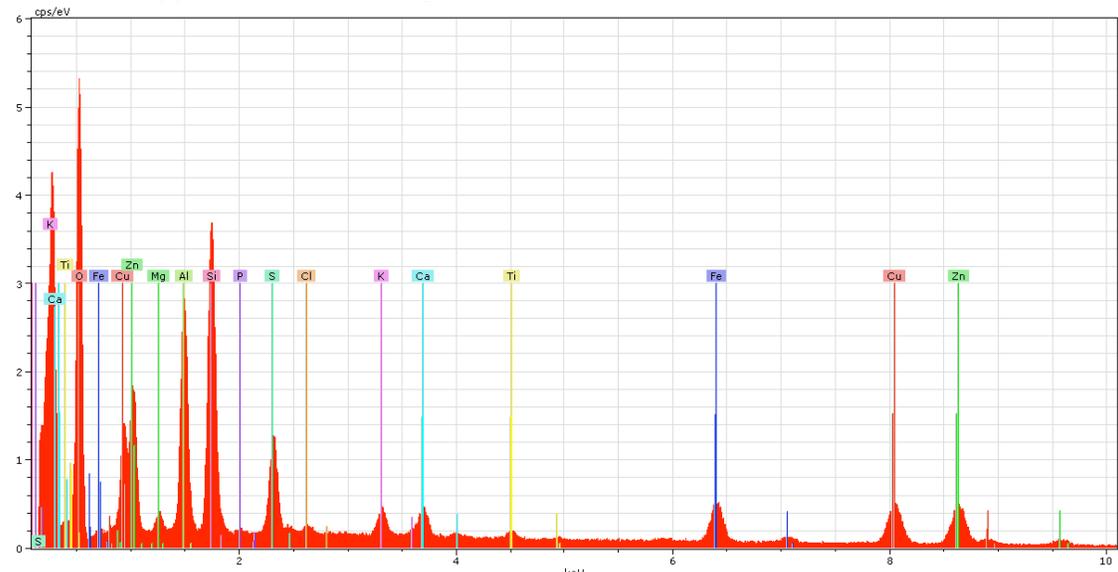


Silica

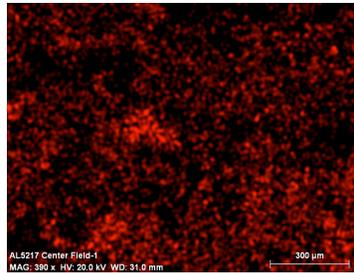


Calcium

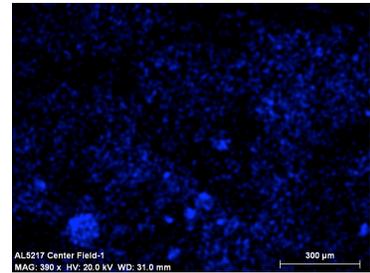
5217_6 central stippled field corrosion product



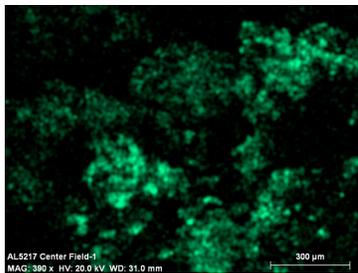
Zinc



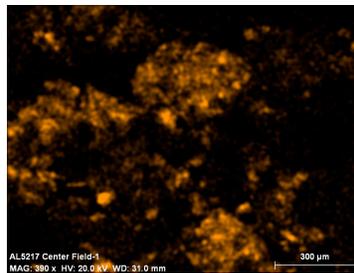
Copper



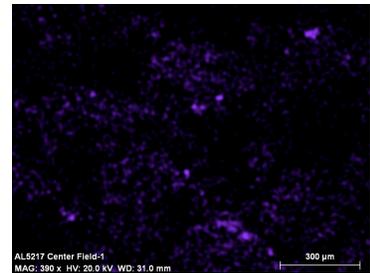
Iron



Aluminum

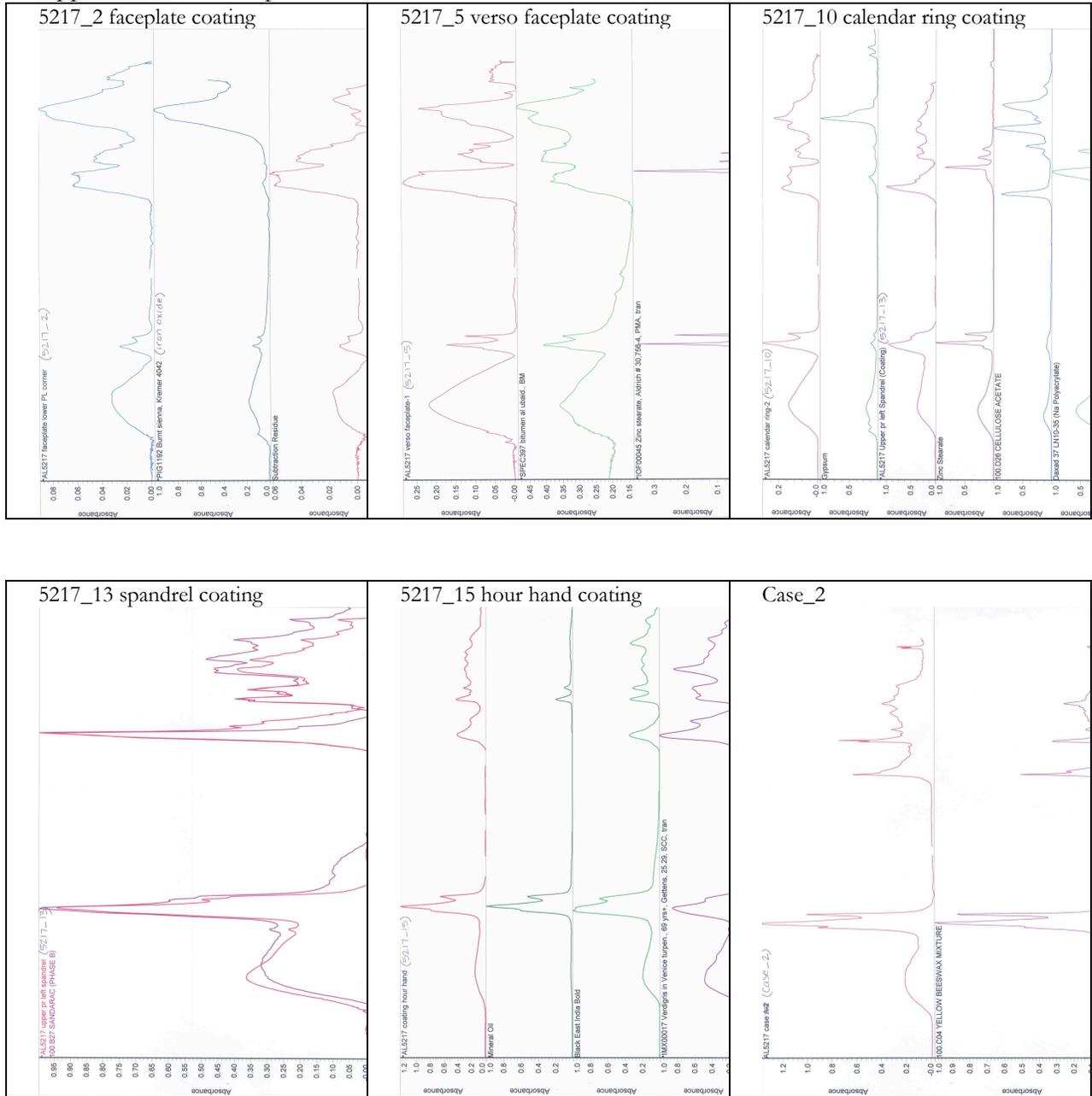


Silica

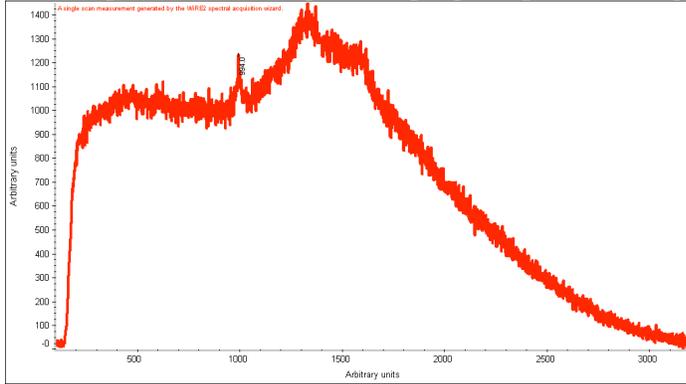


Magnesium

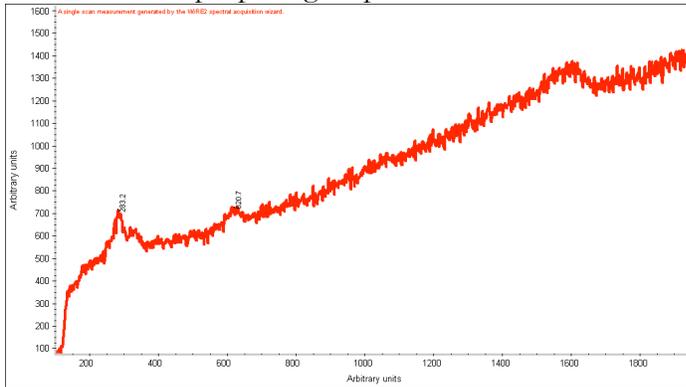
Appendix D: FTIR spectra



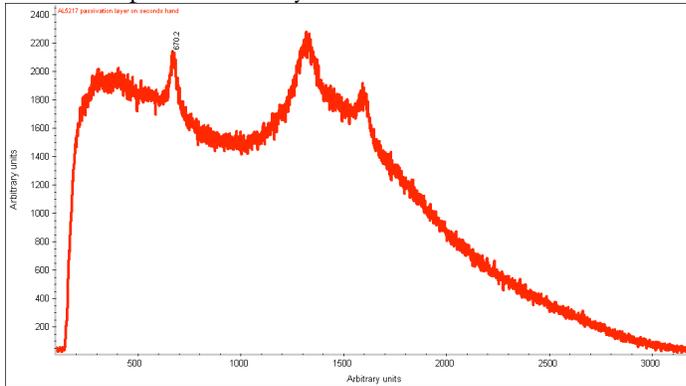
Appendix E: Raman spectra
5217_1 green corrosion product proper right side faceplate



5217_14 lower proper right spandrel



5217_CC passivation layer on seconds hand



Appendix F: GC-MS

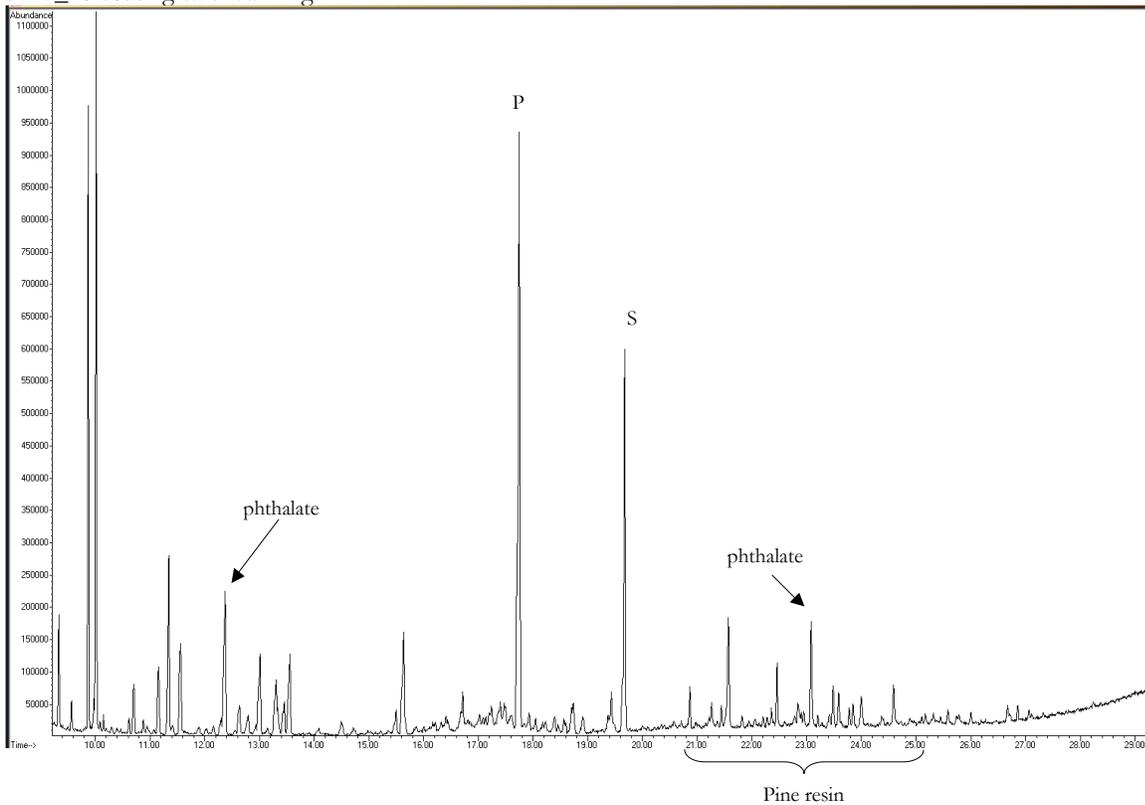
5217_16 black paint hour hand (top)

5217_12 coating upper proper right spandrel (middle)

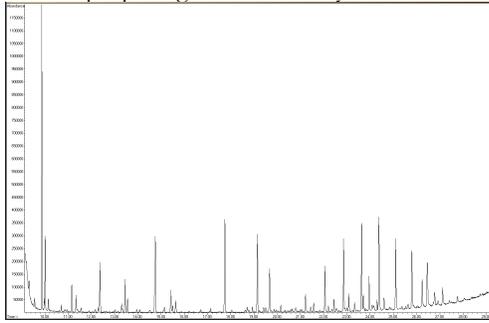
5217_14 coating lower proper right spandrel (bottom)



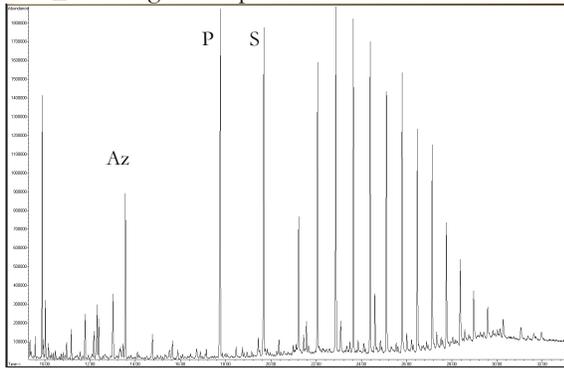
5217_10 coating calendar ring



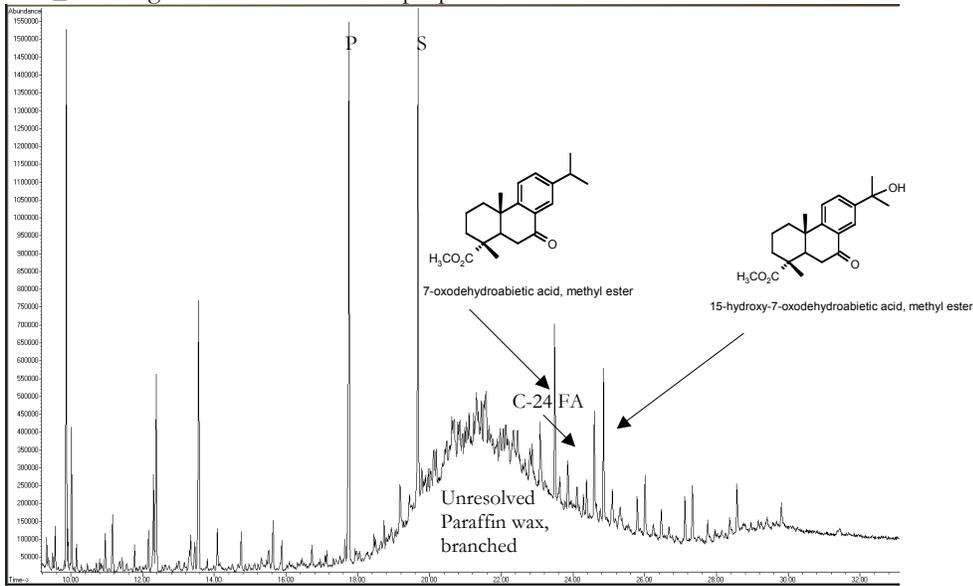
Case_1 proper right front side by foot



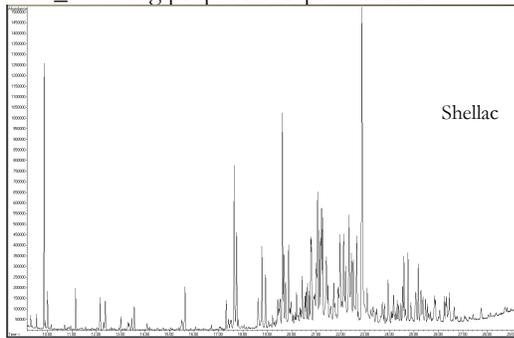
Case_2 coating inner lip of door



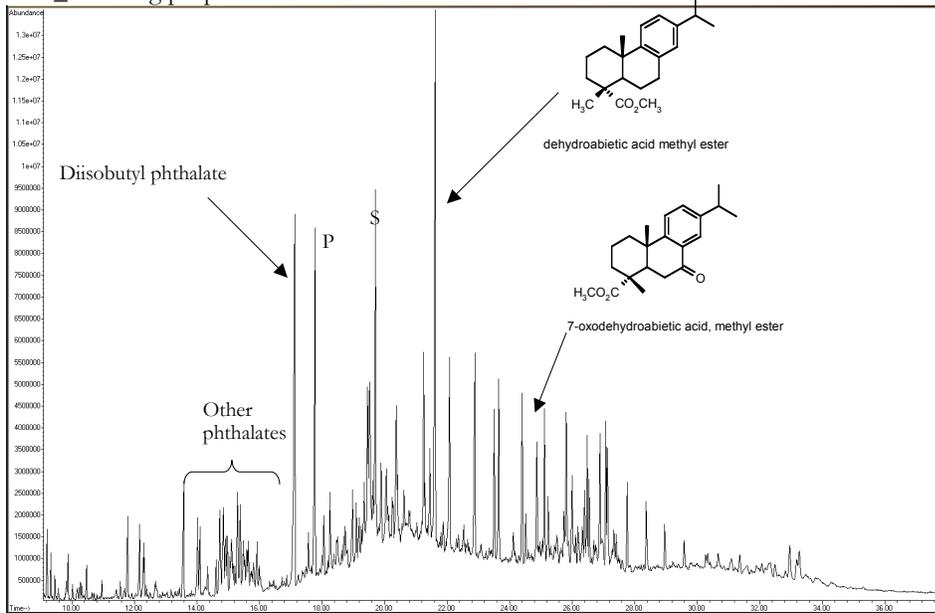
Case_3 coating blanch area beneath proper left rosette on hood



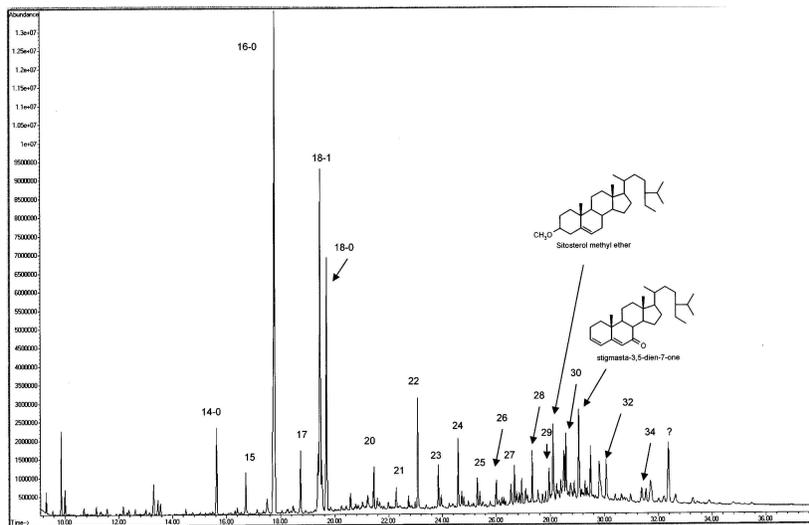
Case_4 coating proper left replacement rosette on hood



Case_5 coating proper left fretwork of hood



5217_4 coating on recto of faceplate

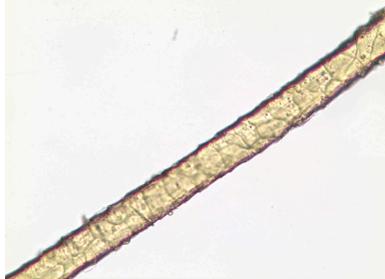


AL5225 - N-methylpyrrolidone extract - second extraction with hexane - MethPrep treatment

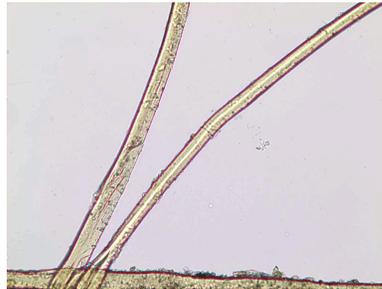
The mix of even and odd fatty acid esters in significant amounts beyond C-18 and the plant sterols suggest carnauba wax
The high level of oleic acid (18-1) may be part of the formulation in a commercial carnauba wax product

Appendix G: PLM photomicrograms

Fiber_1 tan warps and yellow wefts from back of soundboard



Tan warp, 400x visible light

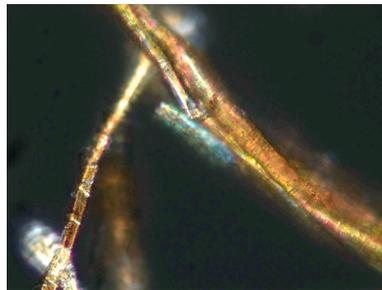


Yellow weft, 400x visible light

Fiber_2 tan warps and wefts from spandrel fretwork in hood



Tan warp/weft, 400x visible light



Tan warp/weft, 400X polarized light