An Investigation of Paul Cézanne’s Watercolors
With Emphasis on Emerald Green

ABSTRACT

Nine watercolors by Paul Cézanne in the collection of the Philadelphia Museum of Art were investigated by conducting elemental analysis of major pigments using qualitative energy dispersive x-ray fluorescence (XRF) carried out at the Winterthur Museum. Copper and arsenic, indicative of emerald green, were detected in discolored tan washes on the Philadelphia watercolors, suggesting that emerald green had darkened on several of the paintings. Results of elemental analysis on the other colors revealed that Cézanne favored a fairly restrained palette, about thirteen pigments, but averaged only five pigments on individual pictures.

INTRODUCTION

The primary impetus for investigating Paul Cézanne’s watercolor palette was the apparent darkening of certain green paints found on several pictures in the Philadelphia Museum of Art. Although the investigation focused on the greens, the other major color families were also included in this study. XRF was carried out on several sites on each of the nine Philadelphia watercolors.

Figure 1 illustrates a representative watercolor, The Balcony, marked with the location of each analysis site. Table I shows the elements that were detected on The Balcony and the pigments implied by these results. Abundant amounts of arsenic and copper, indicating emerald green, were detected on this watercolor, both in brilliant green areas and in tan washes. The other pigments suggested by analysis of The Balcony are: viridian, cobalt blue, cobalt-based purple, and organic red. The organic pigments thought to be used by Cézanne were deduced by the absence of detectable elements in the analyzed areas. Color swatches from an 1887 Winsor & Newton catalogue were analyzed as standards. Reports on the other watercolors analyzed, spectra of elemental results, and written summaries, are available through the Philadelphia Museum of Art.

The watercolors to be discussed are: House on the Hill Near Aix (63-181-7)

Aix Cathedral, View from the Studio at Les Lauves (50-134-35)

Rocks and Trees (50-134-33)

Trees and Rocks No. 1 (67-30-18)

Trees and Rocks No. 2 (67-30-19)

The Balcony (43-75-1)

Oranges on a Plate (63-116-20)

Carafe, Table Knife and Unidentified Object (52-61-11)

Olympia (63-181-123)

Many of the Philadelphia watercolors are landscapes of views in Aix-en-Provence, such as House on the Hill Near Aix, 1895-1900. Throughout his life, Cézanne moved between his home in the south of France and Paris. In 1902 he completed building the studio at Les Lauves, just outside the town of Aix, where he worked until his death in 1906. Aix Cathedral, View from the Studio at Les Lauves, 1902-1904, depicts a scene that is still visible from a point just down the hill from his studio. Bibémus quarry is also in the vicinity of Aix and it was a favorite painting spot of Cézanne, who rented a hut there in 1895. The three Philadelphia watercolors that show his interest in the subject of rocks and trees and could have been painted at Bibémus are: Rocks and Trees, 1880-85, Trees and Rocks No. 2, ca., 1890, and Trees and Rocks No. 1, ca., 1895. The other watercolors in this study include two late works that were probably executed in Aix, The Balcony, ca., 1900, and Oranges on a Plate, ca., 1900; a sketchbook page, Carafe, Table Knife and Unidentified Object, ca., 1882; and an early work, Olympia, ca., 1877.

Cézanne’s watercolor technique allowed the image to unfold in a subtle interplay of overlapping strokes of color wash. Superimposed patches of color combine to create additional colors; rarely were paints mixed on the palette before application to the paper. Graphite pencil lines often play a major role in the composition, defining and supporting...
Fig. 1. The Balcony (43-75-1) with marked sites for x-ray fluorescence analysis. The results corresponding to the locations are noted on Table I
Table I. Results of x-ray fluorescence analysis of *The Balcony*

<table>
<thead>
<tr>
<th>LOCATION (see Fig. 1)</th>
<th>COLOR</th>
<th>ELEMENTS</th>
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<tr>
<td></td>
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the structure. The color of the paper support is also integral to the composition and its discoloration has had an impact on the color balance in some pictures, such as *Oranges on a Plate*, where severe paper discoloration has camouflaged the delicate nuances of transparent color washes. On the verso of many sheets is a second watercolor, often a loose sketch. In choosing sites for analysis, care was taken to select areas where colors did not overlap each other or correspond to painted areas on the verso.

Cézanne often exchanged his paintings for paints and canvases with Père Tanguy, a picture dealer and paint merchant who displayed Cézanne’s paintings in his small shop in the Rue Clauzel, Paris. It’s not known if Cézanne obtained his paint exclusively from Tanguy, or if he traded mainly for the more expensive oil paint and obtained watercolor paint elsewhere. Nor is it known who supplied him with materials after Tanguy’s death about 1893. Dominique Sennelier, of Sennelier Beaux-Arts Distribution, has seen invoices for oil paints sold to Cézanne by his grandfather, who became a color merchant in 1887. According to Sennelier, watercolors available in France were primarily manufactured by a relatively small number of companies: Sennelier, Lefranc & C., Le Bourgeois Aine, P.C. Lambertye-J.M. Paillard (student grade), and English companies such as Winsor & Newton and Rowney & Co. English watercolor paints were readily available in France during this period: Sennelier catalogues advertised the sale of watercolors by English manufacturers and Winsor & Newton printed catalogues in French.

Watercolor paints listed in French and English trade catalogues, from the late nineteenth and early twentieth centuries, helped to confirm the pigments indicated by elemental analysis. Supplementary information was gathered from still existing manufacturers, such as Lefranc & Bourgeois, Sennelier, and Winsor & Newton. Cézanne’s use of the pigments suggested by analysis was further substantiated by lists of colors on the front and back covers and neighboring pages of his sketchbooks, as well as the colors mentioned in his published letters. Additional comparison was made to the pigment study of ten Cézanne oil paintings at the Philadelphia Museum of Art by Marigene Butler.

Table II contains the pigments thought to be present on each watercolor, as deduced from elemental results by XRF. Following is a summary of the pigments that comprise Cézanne’s watercolor palette as suggested by this investigation, including brief remarks on their chemistry and historical background.

**GREEN PIGMENTS**

Green was emphasized in this study, not only because it has darkened but also because it was employed liberally, particularly in his many landscapes. The three green pigments established by the elemental results of XRF were emerald green, viridian, and mixed green.

**Emerald Green (Vert Véronèse, Schweinfurt Green, Paris Green)**

Figure 2 shows an XRF spectra for emerald green, copper aceto-arsenite (Cu(CH₃COO)₂·3Cu(AsO₂)₂), displaying peaks for arsenic and copper. Analysis detected generous amounts copper and arsenic, indicating the presence of emerald green on all the Cézanne watercolors in this study. It was also one of the most commonly found pigments on Cézanne's oil paintings in Butler’s investigation.

Emerald green has darkened to varying degrees on many but not all of the Philadelphia watercolors. In several, the darkened emerald green is accompanied by other signs of deterioration, such as faded organic pigments or discolored paper, as in: *Trees and Rocks No.1, Trees and Rocks No.2, Rocks and Trees*, and *Oranges on a Plate*. In contrast, emerald green paint on *Carafe, Table Knife and Unidentified Object* remains brilliant, even though the paper support was discolored severely. In *The Balcony*, and *Aix Cathedral, View from the Studio at Les Lauves*, only the thinner washes of emerald green have discolored to a dull tan, while the areas of thicker application have remained bright.

**Visual Characteristics of Emerald Green Watercolor**

Emerald green is a brilliant, mint-colored green, as can be seen in color swatches in early trade catalogues. Microscopic examination often reveals a characteristic granular quality due to the paint's near insolubility in water. Deteriorated emerald green may appear as a tan wash often containing bright green particles, that can accumulate and form a ridge along the edge of a puddle of wash.

In some cases, deteriorated emerald green has penetrated through the paper, staining the verso light brown. The two Philadelphia watercolors which exhibit this phenomenon are *Rocks and Trees*, and *Trees and Rocks No.1*. Conversely, in some instances, various watercolor pigments that include emerald green seem to have protected paper from discoloration so that paper behind the painted areas remains lighter than the surrounding paper on the verso. The latter phenomenon can be found on *Oranges on a Plate, Trees and Rocks No.2* and *Carafe, Table Knife and Unidentified Object*.

An additional clue for distinguishing emerald green is given by ultraviolet light examination. Green or tan washes of emerald green that appear pale by visual light will absorb ultraviolet light in the same manner as thicker applications of the paint and look very dark. In contrast, the other green pigments found in this study (viridian and mixed green) do not absorb ultraviolet light to the same degree.
History of Emerald Green

Emerald green was first formulated from arsenic and verdigris in Schweinfurt, Germany, 1814, by Russ and Sattler who were trying to improve upon Scheele's green (copper arsenite). The manufacturing process was published in 1822 separately by Justus von Liebig and André Braconnnot. Under the name Paris green, it was introduced as the first chemical insecticide around 1867. The highly toxic nature of emerald green lead Winsor & Newton and many other manufacturers to withdraw it from production in the 1960's.

The French term *vert Véronèse* refers to emerald green, whereas the French term *vert émeraude* refers to the English pigment viridian. Presumably due to the confusing translation, many French and English nineteenth century trade catalogues transposed the names for emerald green and viridian. However, by the early twentieth century, the translations of these terms, as found in trade catalogues and artists' manuals, appear generally consistent.

Permanence Testing of Emerald Green

Emerald green was one of the watercolors tested for permanence during the late nineteenth century. This includes the Russell and Abney report of 1888 and the Winsor Newton 1892 permanence ratings. Emerald green was rated as moderately permanent, showing slight darkening. George Field stated that all copper greens have a tendency to blacken in impure air, although he thought emerald green was the most durable of this class of pigments. In a 1889 report for George Rowney, emerald green was listed as turning brown when exposed to hydrogen sulfide. The trade catalogues of the period also warned that mixing copper greens with pigments containing sulfides would risk blackening the mixture. Emerald green was included in recent research on the degradative action of copper green pigments on paper, although results on emerald green were inconclusive.

Viridian (Vert Émeraude, Guignet's Green)

Viridian (Cr₂O₃·2H₂O), hydrous oxide of chromium, is typically a transparent bluish-green color and is considered permanent. It was first manufactured in 1838, Paris, by Panetier and patented by M. Guignet in 1859. The determination of chromium by XRF indicated the presence of viridian on five of the watercolors analyzed: *Trees and Rocks No.1, Trees and Rocks No.2, House on the Hill Near Aix, The Balcony,* and *Aix Cathedral, View from the Studio at Les Lauves.* The pigment was not detected on watercolors in this study that have been dated before 1890. Significant peaks for copper and arsenic were found in addition to chromium in analyzed areas on two watercolors, suggesting that emerald green may have been added to viridian on the palette. Cézanne employed viridian sparingly, as complimentary accents to more lavishly used emerald green. The sparse use of viridian may be due in part to the fact that it was almost twice as expensive as emerald green.

Mixed Green

XRF detected cobalt, chromium, and lead in the three isolated strokes of paint in the upper left of *Rocks and Trees,* suggesting a mixed green paint composed of cobalt blue and chrome yellow. This is one of the few paints that Cézanne may have intentionally mixed on the palette; or he could have purchased it premixed under the name cobalt green. George Field stated that cobalt greens were of two types, a mixed compound of cobalt blue and chrome yellow, and a pigment prepared from cobalt and zinc, called Rinmann's green. The former was likely a cheaper substitute for the latter.

BLUE AND PURPLE PIGMENTS

The blue pigment indicated by XRF on most of the watercolors in this study was cobalt; ultramarine blue is thought to be present on one painting. Two different compositions of purple were indicated, a cobalt-based purple, and purple areas that did not yield detectable analytical results.

Cobalt Blue (*Bleu de Cobalt*)

Cobalt was detected by XRF in blue color areas indicating the presence of cobalt blue, cobalt aluminate (Co₃Al₂O₆), on all of the watercolors except *House on the Hill Near Aix.* The discovery of cobalt blue was first published by Thenard, 1803, France; it was generally thought to be stable, although Field was doubtful of it's durability. Examination of the spectra indicate that cobalt blue may have been mixed with other colors on the palette, possibly as a means of extending the costly pigment. In four pictures, *Olympia, Carafe, Table Knife and Unidentified Object, Trees and Rocks No.1,* and *The Balcony,* strong peaks for copper and arsenic, indicative of emerald green, are found in addition to cobalt. In two pictures, *Trees and Rocks No.1* and *Oranges on a Plate,* peaks for lead are found on the spectrum for cobalt, suggesting an admixture of white lead. White lead was found elsewhere on *Oranges on a Plate,* and white particles were visible in the blue paint layer.

Ultramarine Blue (*Bleu Outremer*)

For a number of analyzed blue areas on *House on the Hill Near Aix,* no elements were detected, implying the presence of ultramarine blue or indigo. Ultramarine is the more likely candidate because it was frequently found on Cézanne's oil paintings and color lists, whereas indigo did not occur. Butler identified artificial ultramarine on a number of Cézanne oil paintings, and many listings of bleu outremer exist in the artist's
sketchbooks. When compared to the hand-painted color swatches from an early Winsor & Newton catalogue, the blue wash of House on the Hill Near Aix appeared closer to the swatch of ultramarine than indigo. Factories for the production of synthetic ultramarine, sodium aluminum silicate with sulphur (Na₈₋₁₀Al₆₋₈Si₆O₂₆S₂₋₆) appeared in France shortly after 1828, the date that an award for the manufacture of synthetic ultramarine was given to Guimet by the French government.

Mixed Purples
Two kinds of purples were found, those that contain cobalt, and those that had no detectable elements revealed by XRF. Purple containing cobalt was found in three watercolors that also showed areas of cobalt blue: Rocks and Trees, Oranges on a Plate and The Balcony. These purple areas were likely a mixture of cobalt blue and organic red, or cobalt violet. Although cobalt violet, cobalt phosphate (Co₃(PO₄)₉) or cobalt arsenate (Co₃(As₂O₄)₃), was an unusual and expensive pigment, it was found by Butler on Cézanne’s last great oil painting, Large Bathers. The fading pattern on Oranges on a Plate, a watercolor that exhibits peaks for cobalt in both blue and purple washes, invited speculation of a mixed purple. A patch of purple that was partially protected by a mat has faded to blue in the exposed portion, as if the fugitive red component had been lost.

Purples on Carafe, Table Knife and Unidentified Object and House on the Hill Near Aix were analyzed but did not contain detectable elemental information, and are thought by conjecture to reflect organic purple or a mixture of ultramarine and organic red. The latter watercolor also contains blue areas thought to be ultramarine. Neither cobalt violet or an organic purple, such as purple lake, were found in the artist’s writings.

YELLOW PIGMENTS
The three yellow pigments implied by elemental results of XRF analysis in this study are chrome yellow, iron oxide yellow and organic yellow.

Chrome Yellow (Jaune de Chrome)
Chrome yellow, lead chromate (PbCrO₄), shows peaks for chromium and lead by XRF. Elements for chrome yellow were detected in the mixed green in Rocks and Trees, as previously mentioned, and in a yellow highlight in Oranges on a Plate. Chrome yellow came into commercial production around 1820; it is not stable and was known to darken and become greenish.

Iron Oxide Yellow/Orange
The presence of iron was confirmed by XRF in yellow and orange areas on five of the watercolors analyzed:

Olympia, Carafe, Table Knife and Unidentified Object, Rocks and Trees, Aix Cathedral, View from the Studio at Les Lauves and Oranges on a Plate. Since peaks for iron were found in all of the watercolor papers, the spectrum peaks thought to indicate iron oxide pigment were necessarily stronger than the iron peaks detected by the paper alone. The iron oxide yellow is likely yellow ochre (Fe₂O₃·H₂O) and the orange, burnt sienna; both were mentioned numerous times in the lists in Cézanne’s sketchbooks.

Organic Yellow
The absence of elements detectable by XRF in yellow areas suggested an organic yellow. The pigment may be gamboge, a gum resin produced from varieties of Garcinia, an evergreen tree found in southeast Asia. Gamboge, gomme-guite in French, was the only organic yellow included in Cézanne’s lists of colors. The organic yellow could also be a yellow lake which was thought to occur in combination with iron oxide yellow in Butler’s study of Cézanne’s oil paintings. Organic yellow was found on two watercolors: Trees and Rocks No.2 and House on the Hill Near Aix. On the latter watercolor, analyzed orange areas that did not show detectable elements, by supposition, could be a mixture of organic yellow and organic red.

RED PIGMENTS
The three red pigments that were suggested in this study were red lead, vermilion, and organic red.

Red Lead (Rouge de Saturge)
XRF analysis detected lead in an area of red paint on Rocks and Trees, indicating the pigment red lead, lead tetroxide (Pb₃O₄). Red lead was usually present as rouge de saturre in French catalogues, but was not common in Winsor & Newton trade catalogues. It was not a durable watercolor pigment; Church calls the use of red lead in watercolor as “inadmissible.” Red lead is rarely cited in the other studies; once in Butler’s work on Cézanne’s oil paintings, and as a single written notation in the artist’s color lists.

Vermilion (Vermillion)
Vermilion, mercury (II) sulphide (HgS), displays peaks for mercury in XRF spectra. Mercury was detected in areas of red wash, suggesting the presence of vermilion on three watercolors: Olympia, Rocks and Trees, and Oranges on a Plate. Peaks for lead accompanied mercury in two watercolors; red lead and white lead were found on other areas of Rocks and Trees and Oranges on a Plate, respectively, and could have been mixed with vermilion by the artist. Alternatively, red lead could have been added by the manufacture. Harley mentions that not only was vermilion sometimes adulterated by the manufacturer with organics or red lead, but
vermilion was sometimes added to carmine to improve the latter's permanence; a combination of vermilion and carmine was marketed as scarlet lake.\textsuperscript{22}

**Organic Red**

XRF analysis of red wash on six watercolors implied the presence organic red by the absence of detectable elements. These watercolors were: *Olympia, Trees and Rocks No. 1, Trees and Rocks No. 2, House on the Hill Near Aix, The Balcony, and Aix Cathedral, View from the Studio at Les Lauves.* Cézanne mentioned various madders and lakes in his letters and sketchbooks: *laque garance foncée, garance rose, laque fine, laque brûlée.* When viewed by ultraviolet light, the organic reds on the Philadelphia watercolors did not fluoresce, ruling out madder and thus supporting the presence of alizarin or carmine lakes. Carmine or crimson lake, made from the dried bodies of scale insects (cochineal or kermes), was one of the least permanent watercolors listed by the Russell and Abney report of 1888.\textsuperscript{23} Alizarin (1,2 dihydroxyanthraquinone), first reported as synthesized by Graebe and Lieberman, 1868, Germany, is said to have replaced madder as it was considerably more light-fast and half the price of both madder and carmine. Alizarin was present on every period watercolor list in English trade catalogues, however the name was not found in French catalogue color lists, which remained dominated by madder and carmine lakes.

The red wash in *Aix Cathedral, View from the Studio at Les Lauves*, contained a minor iron peak that could represent iron oxide red (light red). However, this area did not appear similar to color swatches of light red in an early Winsor & Newton catalogue.\textsuperscript{24}

**CONCLUSION**

Analysis indicated that many strokes of tan wash that occurred on the Cézanne watercolors in this study were actually patches of previously bright emerald green watercolor that had deteriorated and darkened, as supported by the presence of copper and arsenic by XRF. Every watercolor painting showed the presence of emerald green, often in abundant amounts. With the exception of *House on the Hill Near Aix* and *Olympia*, most of the watercolors exhibited some degree of emerald green deterioration. Discoloration of emerald green is most apparent in thin washes, while thicker areas of paint often remain brighter green.

Table I lists thirteen individual pigments that were probably in Cézanne's watercolor palette, plus one mixed green. The results of the investigation suggest a few general trends in Cézanne's use of certain pigments. Cobalt was the second most frequently detected pigment, found in all but one of the watercolors. The other most commonly used pigments appear to be iron oxide yellow and organic red (determined by the absence of detectable elemental results). Viridian was used only after 1890, and then sparingly. An average of five different pigments is indicated on each watercolor. For instance, on the illustrated painting, *The Balcony*, emerald green, cobalt blue, viridian, organic red and a cobalt-based purple are indicated.

Many of the analyzed strokes of paint were found to be composed of relatively pure pigments, straight from the cake or tube, with few deliberate mixtures. The only identified mixture was a green found on one painting, thought to be composed of chrome yellow and cobalt blue. Speculated mixtures of other secondary colors are: purples that are possibly created from an organic red plus cobalt or ultramarine blues; and orange which may be composed of organic red and yellow. Vermilion may have been mixed with minor amounts of red lead by the artist, or it may have been adulterated by the manufacturer. Significant signals for copper and arsenic found on spectra for cobalt and viridian suggest an admixture of emerald green, either intentionally by Cézanne, or accidently from a messy palette. Trace amounts of arsenic and copper that registered in other colors are most likely from residual emerald green paint on the artist's brush.

The watercolor pigments suggested in this study generally were consistent with other citations, including Butler's analysis of ten oil paintings, and the names of paints found in the artist's sketchbooks and letters. Orpiment, Indian yellow, terre verte, and prussian blue, also cited in the forementioned, were not found in this study. Additionally, although madders were frequently mentioned in his sketchbook lists, they were absent from the watercolors.

**ACKNOWLEDGMENTS**

This project would not have been possible without the analytical expertise of Beth Price, Janice Carlson and Andrew Lins, as well as the art historical support of Joseph Rishel. The author would also like to extend appreciation for the continued support of the Conservation Department of the Philadelphia Museum of Art, especially Nancy Ash and Marigene Butler.

**NOTES**

1. XRF was executed by Janice Carlson and Beth Price using a Kevek Instrument 0750 at the Winterthur Museum. The secondary target was usually carbon, however germanium was used on a few sites. The number of sites tested on each picture varied from six to nineteen areas, depending upon the complexity of the composition. The paper and matboard of each watercolor was also analyzed and the discussion of the pigments is limited to the elements that are in addition to those found in the watercolors.
<table>
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<th>Olympia c.1877 63-181-123</th>
<th>Carafe c.1882 52-61-11</th>
<th>Rocks &amp; Trees 1880-5 50-134-33</th>
<th>Trees 2 c.1890 67-30-19</th>
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<td>Organic yellow/orange</td>
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<td>Vermilion, HgS</td>
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<td>Organic red</td>
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<td>Red lead, PbO₄</td>
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<td>Lead white</td>
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<td>2PbCO₃ • Pb(OH)₂</td>
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Table II: Pigments indicated on nine watercolors by Paul Cézanne.
Fig. 2. Spectrum of qualitative energy x-ray fluorescence detection of copper and arsenic, indicating emerald green pigment on *The Balcony* (43-75-1)
2. The XRF equipment used for this study did not detect elements with atomic weights higher than potassium on the periodic table. Supplemental analytical methods, such as scanning electron microscopy, x-ray diffraction, Fourier transform infrared spectroscopy, and high pressure liquid chromatography were not used for further identification. These methods required destructive sampling techniques that were not safely possible on thin watercolor washes, whereas destructive sampling was not necessary for analysis by XRF.


5. Private conversation.


9. A correlation between paper quality and the darkening of emerald green has not been established. Preliminary fiber analysis of the paper supports of the nine watercolors in this study has identified a content of mostly rag fiber with trace amounts of grass. The identifiable watermarks are from the Canson & Montgolfier papermill.


12. It appears that viridian was referred to as *Vertonese* green in a number of late nineteenth century catalogues that translated French and English terminology. For example, Winsor & Newton catalogues described viridian as synonymous with Veronese green. But, a 1904 trade catalogue from Sennelier, French artists manuals, L'Aquarelle by Karl Robert (Paris, 1911) and *L'Art de Peindre Les Paisages à l'Aquarelle* by G. Fraipont (Paris), and in *The Chemistry of Paints and Paintings* by Sir Arthur Church (London: 1915).


14. The "Composition of Pigments" and "A Classification of Winsor and Newton's Watercolours in Three Degrees of Permanence" were published initially in 1892 by Winsor & Newton, Limited, and appeared in company trade catalogues after that date.


18. Field and Davidson, p.73.


20. Taylor, op. cit..


24. Taylor, op. cit..

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FAITH ZIESKE
Associate Conservator for Works of Art on Paper
the Philadelphia Museum of Art