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X-Ray fluorescence as a method of characterizing inorganic pigment patterns in the work of Julian Onderdonk

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ABSTRACT

This study utilized portable X-Ray fluorescence to analyze pigment patterns in 33 paintings by Julian Onderdonk, a 19th-20th century Texas impressionist. This analysis led to the identification of distinctive pigment preferences for Onderdonk at different periods of his career. Using the pigment preference patterns identified in the paintings that were dated by the artist, undated works were analyzed and assigned to different periods in the artists career based on their pigment patterns. This study represents a non-destructive method for organizing the artist's work without solely relying on stylistic changes.

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1. Introduction

Robert Julian Onderdonk (1882–1922), commonly known as Julian Onderdonk, was an American Impressionist painter from San Antonio, Texas. He is best known for his vibrant, sprawling depictions of bluebonnet-filled Texas landscapes, and his paintings have been showcased in museums and art galleries around the United States, even adorning the White House walls during the presidency of George W. Bush from the years 2000–2008 [1,2].

Originally from Texas, Onderdonk studied art at the Art Students League in New York City from 1901 to 1909, and while he sold his work the best he could, like many aspiring artists he struggled financially. In 1904, Onderdonk began a business relationship with someone known only as Chas. Tunison, (likely either Charles or Chase), who paid Onderdonk to paint and then sold the paintings on his own. The paintings that Onderdonk did for Tunison were signed under a pseudonym of Chas. And Chase Turner. The Turner paintings are indistinguishable from the work that Julian Onderdonk signed with his own name; often they are of the exact same subjects and scenes. By having him use a pseudonym and selling the work without his presence, Tunison was able to keep Onderdonk reliant on him without any alternative source of income for at least four years. By 1908, Onderdonk had either completely eliminated or at least severely limited his relationship with Tunison and began signing his own name to his work once again [3].

The revelation that Chas. Or Chase Turner was a pseudonym for Onderdonk was made by Texas art historian James Baker, who published his findings in the 2014 book Julian Onderdonk in New York: The Lost Years – The Lost Paintings. The paintings analyzed in this study cover the three major periods of Onderdonk's work, ranging from his pre-New York phase in 1899, through his time in New York from 1901 to 1909, followed by his time back in Texas from 1909 up to the very last painting he completed before his death in 1922.

Baker possessed or had access to 33 paintings signed both as Onderdonk and Turner, ten of which were undated and two of which

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had only tentative dates based on associations with similar, dated works. Analysis of Onderdonk's signature revealed a shift in style between 1906 and 1908, allowing some of the undated works to be grouped to a general date range [3]. To further narrow down the dates, this study utilized portable energy dispersive X-Ray fluorescence (pXRF) analysis to attempt to identify pigment markers that can further refine these groupings, and to develop pigment patterns that are unique to certain periods of Onderdonk's career. There has been a growing need for non-destrcutive in situ analysis of pigments, and the non-invasive, non-destructive nature of pXRF analysis was essential to gain access to the paintings for this study [4,5]. By then comparing the pigment patterns in these refined groups to the undated works, date ranges can be assigned with greater certainty than stylistic comparisons.

2. Methods

For each painting analyzed, several small areas were chosen to examine based on pigment hue, apparent homogeneity of the paint, and the thickness of the paint. Data was obtained with a Bruker Tracer III-SD pXRF detector, and analyzed in Bruker's S1pXRF software. The spectra for the different points were compared to one another in order to attempt to isolate the constituent elemental building blocks responsible for a particular hue. In some cases, a distinct pigment color was determined, and in others, the colors were clearly a blend of two or more colors. Though some of the pigments analyzed remain ambiguous, like other similar studies, for the most part this method of analysis was successful [6–8].

There are two major drawbacks to using pXRF to analyze pigments. The first is that the Bruker pXRF instrument is unable to detect organic elements due to the low fluorescence energy levels of low Z-number elements [9]. This means that the analyses presented here are likely incomplete. A number of organic based pigments exist and are frequently used, but given the inability of the instrument to detect them, they were necessarily ignored for this study. In some cases, it is noted that due to a lack of otherwise compelling data, organic pigments are the most likely source of a color, but this is inference based on a lack of evidence.

The second drawback is that fundamentally, XRF analysis is unable to detect chemical structure. The elemental composition is read, but the chemical bonds between the elements are not [10,11]. Many elements are present in a wide variety of pigments. Iron (Fe) for example can be found in hematite red, orange and yellow ochre, and even Prussian blue [12]. When each pigment point is analyzed, the hue of the point must be taken into account when attempting to find the best chemical fit for the elements present. Table 1 below summarizes the pigments identified in this study with their chemical formula and earliest known use.

2.1. Sample painting analysis

Elemental data points were collected across all 33 paintings, then collated and compared. An example of how the analysis was carried out across the assemblage can be seen here with the 1922 painting *Dawn in the Hills* (Fig. 1). Apart from being a particularly beautiful painting in its own right, *Dawn in the Hills* is highly treasured due to the fact that it is the last painting that Onderdonk ever painted [15].

A total of seven points were analyzed for this painting. Points 1 and 2 are the whites of the sky, points 3 and 4 are blues, point 5 is the green of the tree to the left of the painting, point 6 is the reddish background in the lower left-hand corner, and point 7 is the signature. This painting was framed and unable to be removed from the frame, but for those that were unframed or able to be removed

Table 1
Pigments, their chemical formulas, and use for artworks [13,14].

Pigment name	Chemical Formula	Date
Barium white	$BaSO_4$	Used in Antiquity, manufactured from 1830CE in France
Titanium white	TiO_2	First produced in 1821CE, but not available to artists until the late 1920s CE
Lead white	$Pb_3(CO_3)_2(OH)_2$	At least as old as 1500BCE in Egypt and Greece
Zinc white	ZnO	First produced as early as 1782CE, mass produced by 1835CE
Realgar red	As_4S_4	Used in antiquity
Hematite (or ochre)	Fe_2O_3	Used since prehistoric times
Red lead (minium)	Pb_3O_4	Used since the Roman empire
Vermillion red	HgS	Used in antiquity
Lemon yellow	$BaCrO_4$ or $SrCrO_4$	Discovered in 1809CE
Cadmium yellow	CdS	Discovered in 1817CE
Chrome yellow	$PbCrO_4$	Discovered in 1809CE
Zinc yellow	$ZnCrO_4$	Discovered in 1809CE
Chromium oxide green	Cr_2O_3	Discovered in 1809CE
Cobalt green	Mg_2TiO_4 or Zn_2TiO_4	Discovered in 1809CE
Verdigris green	$Cu(C_2H_3O_2)_2 \bullet {}_2Cu(OH)_2$	Used in antiquity
Azurite blue	$Cu_3(CO_3)_2(OH)_2$	Used in antiquity
Cerulean blue	$CoO{\cdot}SnO_2$	Introduced in 1821, reintroduced in 1860
Cobalt blue	$CoAl_2O_4$	Discovered in 1775, manufactured from 1804 for artists
Egyptian blue	$CaCuSi_4O_{10}$	Used in antiquity
Han blue	$BaCuSi_2O_6$	Discovered in 1859
Prussian blue	$(Fe_4[Fe(CN)_6]_3)$	Known since 1704, manufactured from 1870 for artists
Smalt	Co – doped Si glass	Known since mid-16th century
Cobalt Violet	$Co_3(PO_4)_2$ or $Co_3(AsO_4)_2$	Discovered in 1859

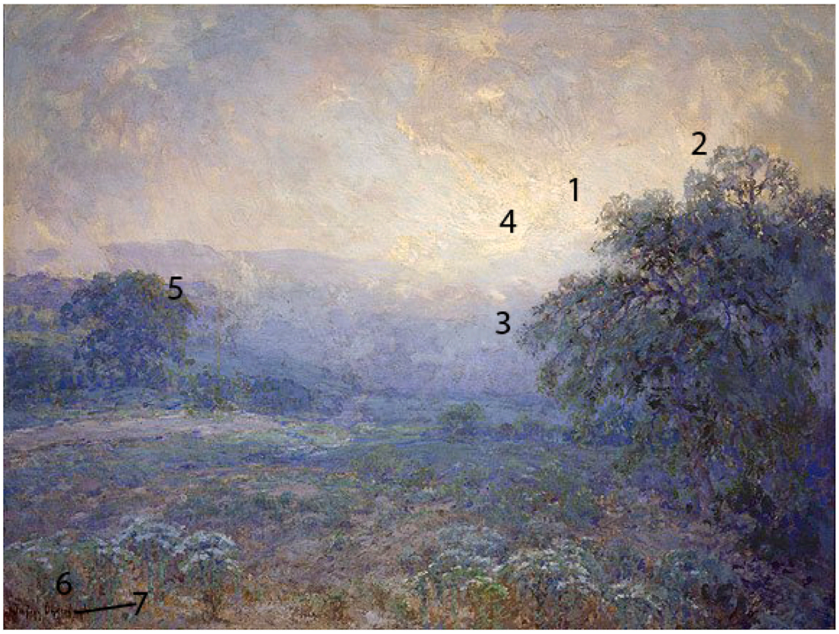

Fig. 1. Dawn in the Hills. 1922, Signed Julian Onderdonk, Oil on Canvas, 30in x 40in, Witte Museum, San Antonio, TX.

from a frame, a portion of non-painted canvas was analyzed to determine the elements present in the primer. After each point was tested, they were analyzed by color grouping.

2.1.1. White

As seen in Fig. 2, the elemental composition of the white of the clouds in points 1 and 2 are predominantly zinc and lead, and therefore are most likely to be a zinc white and a lead white. Both zinc and lead peaks are consistent across all peaks, and so it stands to reason that the painting was primed with both. The presence of calcium and cadmium in the scan are likely due to the blending of paints to achieve a different hue of white. They are found in similar intensities across all spectra.

2.1.2. Blue

Fig. 3 shows that both blues of points 3 and 4 are clearly cobalt based when compared to the white spectrum of point 1. As with the

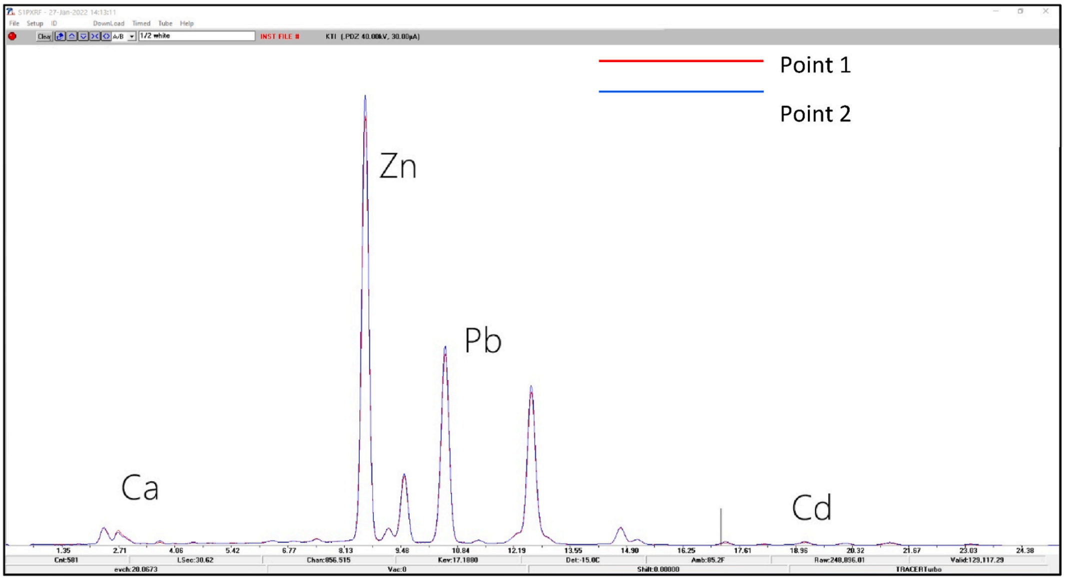

Fig. 2. Dawn in the Hills. Point 1 and 2, white.

rest of Onderdonk's paintings in the 1920s, this cobalt based blue does not have the indicative tin or aluminum peaks that would point toward cerulean blue or cobalt blue. Nonetheless, this cobalt signature is consistent with the other blues in Onderdonk's late period work, and could indicate the use of smalt or ultramarine. The presence of calcium, chromium, and iron are consistent with the background across the rest of the spectra and therefore are not likely part of the blue pigment.

2.1.3. Green

The green of point 5 shown in Fig. 4 is a chromium based green, so it likely viridian, a chromium oxide. Many commonly used greens are copper (Cu) based, like verdigris, emerald green, and malachite, but the lack of a copper peak here rules those out. The presence of calcium, chromium, and iron are consistent with the background across the rest of the spectra and therefore are not likely part of the green pigment.

2.1.4. Red and signature

Fig. 5 shows that the area behind the signature is a reddish orange, which appears to be iron based, indicating hematite. In point 6, there is also a trace of mercury, indicating that the red highlights are vermillion (HgS) instead of iron. Point 7, the signature, has a slightly higher peak for chromium, likely indicating that the red and green were mixed to make a darker color.

For *Dawn in the Hills*, as the spectra were analyzed, the results were added to a spreadsheet for comparison across the collection. As the results continued to build, patterns and trends started to become clear.

3. Results

Table 2 lists each painting with a known date and the characteristic elements for each hue analyzed, with the exception of *Bluebonnets in San Antonio*; this painting had titanium in each point analyzed, indicating that it was primed with titanium white, a paint that was not available until after Onderdonk's death [16]. Additionally, *Milkweed in Bandera* was omitted due to an inability to separate out conclusive elemental data for the different pigments. Based on this table, Onderdonk's preference for zinc white over lead white grew, and by 1914 it seems he had phased the lead white out of use almost entirely until he re-introduced it in 1921. He seems to have eliminated mercuric red pigment by 1908, though it does show up again in the 1922 *Dawn in the Hills*. In 1909 there was a shift away from iron-based blues to cobalt-based blues, along with a shift from zinc-based yellows to cadmium-based yellows.

4. Discussion and conclusions

Despite the limitation of XRF to obtain only elemental data about the pigments used from which the pigments can only be inferred, with enough data points and a moderately restricted pool of possible chemical formulas, it is entirely possible to establish the chemical makeup of cultural resources like art and archaeological artifacts. With the work of Julian Onderdonk, clear patterns of changing pigment preferences through time revealed themselves when each of the paintings was analyzed. It has been shown that undated works can be reasonably associated with the spectral signatures of dated works, allowing for a completely non-destructive way to categorize the undated works into the various phases of Onderdonk's career. It has also been shown that by establishing these patterns, paintings incorrectly attributed to an artist can be discovered, as is most likely the case with *Bluebonnets in San Antonio*.

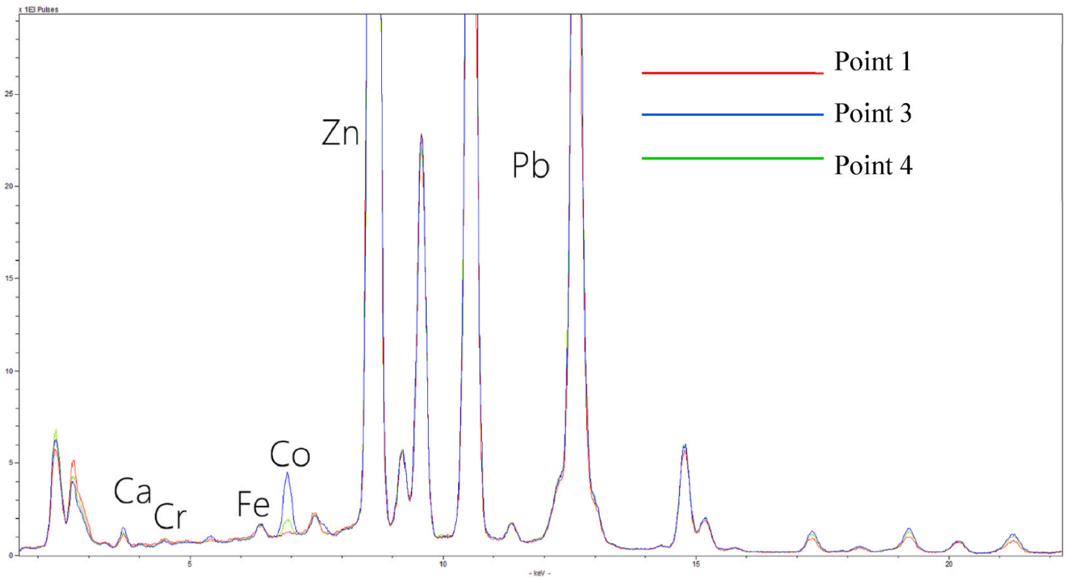

Fig. 3. Dawn in the Hills. Point 1, white, compared to points 3 and 4, blues.

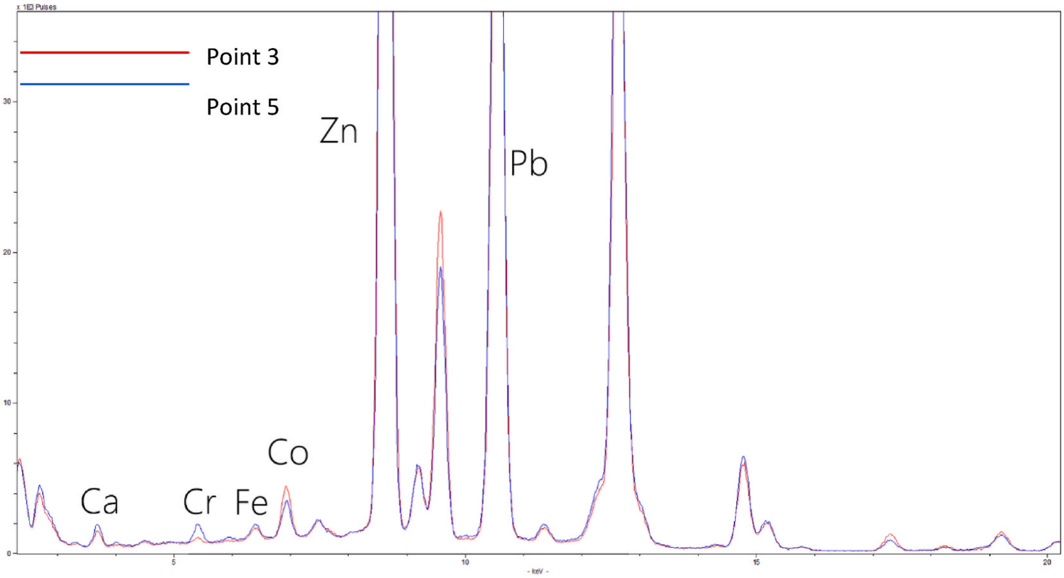

Fig. 4. *Dawn in the Hills.* Point 5, green, compared to point 3, blue.

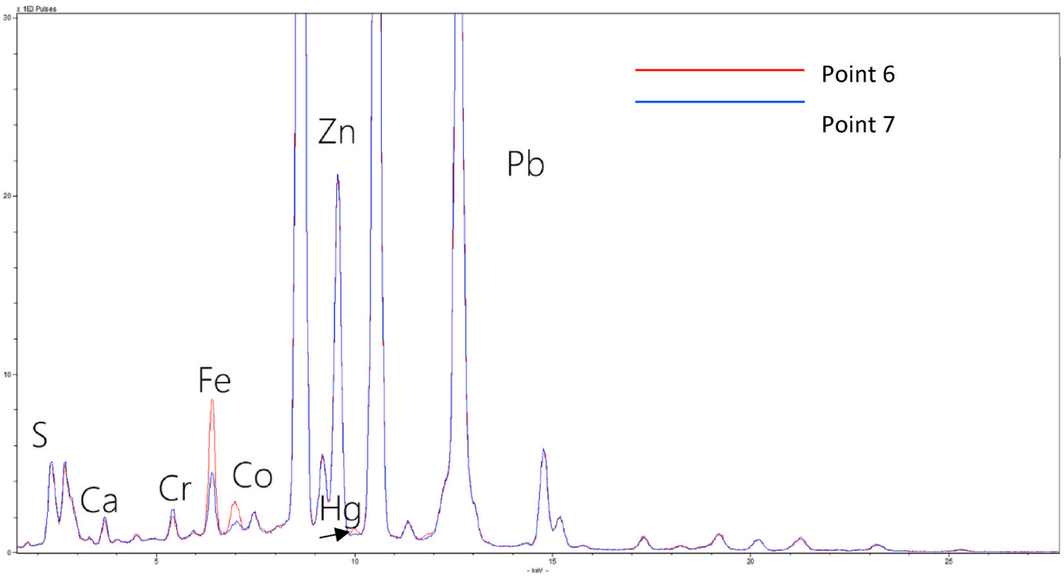

Fig. 5. *Dawn in the Hills.* Point 6, red, compared to point 7, the signature.

The aim of this study was to utilize a portable non-destructive analysis technique to expand the knowledge available about a collection of cultural heritage materials. The results of the study outlined here have proven to be very satisfactory in achieving this aim, though clearly refinements in instrumentation would be advantageous. Future studies incorporating the use of analytic methods capable of detecting organic materials and the chemical bonds between the elements detected would greatly enhance the breadth and depth of the results outlined in this study. However, given that the pXRF was easily transported to the various locations of the paintings and obtained excellent data sets without any adverse effects on these priceless works of art, this was overall a successful endeavor.

Authors contributions

Christopher Dostal, PhD: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Table 2
Dated paintings and their primary elemental constituents for each color.

Painting & Location	Year	Primer	White	Red	Yellow	Green	Blue	Brown
Sunset November 1899 (Private collection)	1899	Pb	Pb	Fe	Zn/Cr	Cu	Cu	
Sand Dunes (Villa Finale Museum, San Antonio TX)	1901	Pb	Pb	Fe/As	Zn/Ba	Cu	Fe	
Cock Fight Amid the Jacals (Private collection)	1905	Pb	Pb	Hg	Fe/Sr	Cr		Fe
Portrait of G. Beddle Moore (Witte Museum, San Antonio, TX)	1905	Pb	Pb	Hg	Zn/Ba			Mn/Fe
Harbor Scene (Private collection)	1906	Pb	Pb	Hg			Fe	Fe
October Sullivan Co. NY (Private collection)	1908	Pb	Pb	Fe	Zn	Cr	Fe	
A June Morning (Private collection)	1909	Pb	Pb	Fe	Zn/Ba	Cr	Fe	
Family at Cards (Witte Museum, San Antonio, TX)	1909	Pb	Pb	Fe	Zn/Cd		Co	
Bluebonnets and Cacti (Villa Finale Museum, San Antonio TX)	1910	Zn/Pb	Zn/Pb	Fe	Sr/Cd	Cr	Co/Fe	
Bluebonnet Field (Witte Museum, San Antonio, TX)	1912	Pb	Pb	Fe	Cd	Cr	Co/Sn	
A Pool on the Guadeloupe (Villa Finale Museum, San Antonio TX)	1913	Pb	Zn/Pb	Fe	Zn	Cr	Co/Sn	
Afternoon Back of Laurel Heights (Witte Museum, San Antonio, TX)	1913	Pb	Zn/Pb	Fe	Zn/Cd	Cr	Co	
Evening in the Bluebonnets (Villa Finale Museum, San Antonio TX)	1914	Zn	Zn	Pb/Fe	Cd	Cr	Co/Sn	
Texas Mountains on Williams Ranch (Villa Finale Museum, San Antonio TX)	1915	Zn	Zn/Ti	Pb/Fe	Cd		Co/Sn	
Williams Ranch, 20 West of Kerrville TX, near Junction (Villa Finale Museum, San Antonio TX)	1915	Zn	Zn	Pb/Fe	Cd	Cr	Co	
Late Afternoon Sunlight on the Bluebonnets (Witte Museum, San Antonio, TX)	1916	Zn	Zn	Fe	Cd	Cr	Co/Sn	
Bluebonnets at Sunset San (Villa Finale Museum, San Antonio TX)	1919–20	Zn	Zn	Fe	Ba/Sr		Co/Sn	
A White Road at Late Afternoon (Witte Museum, San Antonio, TX)	1921	Zn	Zn	Pb/Fe	Ba/Sr	Cr	Co	
Miles and Miles of Bluebonnets (J. Wayne Stark Gallery, College Station, TX)	1921	Zn	Pb	Fe	Sr	Cr	Co	

Using this table as a stepping off point for spectral comparisons between paintings, Table 3 shows the elemental composition of the dated paintings compared to the undated paintings to see which paintings fit with which date range the best. Several paintings illustrate shortcomings in the date ranges derived from the dated paintings; *At the Edge of the Forest* fits best with the 1909 range of pigments, but the inclusion of mercury hints that Onderdonk continued to use mercuric red throughout his entire time in New York instead of stopping in 1906. Likewise, *Seascape V*, signed Chas. Turner, fits best with the dates of 1905–1908, and if this is correct, the supposition that zinc whites were not introduced until 1909 must be incorrect.

Table 3
Undated paintings and their primary elemental constituents for each color.

Painting & Location	Primer	White	Red	Yellow	Green	Blue	Brown
Pastoral with Lady in Red (Private collection)	Pb	Pb	Hg/Fe	Ba	Cr	Fe	Mn/Fe
Seascape V (Private collection)	Pb/Zn	Pb/Zn	Hg/Fe	Ba	Cr	Org	
Landscape with Cacti (Villa Finale Museum, San Antonio TX)	Zn	Zn	Pb	Cd	Cr	Co	
A Man Fishing From a Boat (Private collection)	Pb	Pb	Fe/Hg	Zn/Ba	Cr	Cu	
At the Edge of the Forest (J. Wayne Stark Gallery, College Station, TX)	Pb	Pb	Hg/Fe	Cd/Zn	Cr		
Central Park (Private collection)	Pb	Pb	Fe	Cd	Cr		Fe
Fall Landscape #2(Private collection)	Pb	Pb	Hg	Ba/Sr/Zn	Cr	Cu	
Large Bluebonnet Landscape (Private collection)	Zn	Pb	Fe/As	Cr/Sr	Cr	Cu/Co	
Summer Afternoon (Private collection)	Pb	Zn/Ba	Fe		Cr	Org	Mn
Bluebonnet on a Texas Landscape (Villa Finale Museum, San Antonio TX)	Zn	Pb	Fe	Cd	Cr	Co/Sn	Mn
Study – Lupine (Witte Museum, San Antonio, TX)	Zn	Zn	Pb	Cd/Ba Sr	Cr	Cu/Co	

Despite these shortcomings, the compositions of several of the undated paintings match very well with the dated paintings. *Pastoral with Lady in Red* looks very much like *Cock Fight Amid the Jacals* and *Portrait of G. Beddle Moore*, and it is likely that it was painted around 1905. Table 4 lists the undated paintings with their most parsimonious compositional match to the dated works. To further substantiate the matches made via the elemental composition, the undated paintings were crosschecked with the signature analysis of selected paintings carried out by Baker [3]. There were no conflicts between the assigned date ranges and the signature estimated dates, which, if nothing else is at least encouraging.

Table 4
Undated paintings and their assigned date ranges based on spectral similarities with dated paintings.

Painting & Location	Assigned Date Range	Basis	Signature Estimated Date
Pastoral with Lady in Red (Private collection)	1905	Pb white, Hg red, Fe blue, Mn brown	
Seascape V (Private collection)	1905–1908	Hg red, Org Blue, Ba yellow	
Landscape with Cacti (Villa Finale Museum, San Antonio TX)	1910–1915	Zn white, Pb red, Co blue	
A Man Fishing From a Boat (Private collection)	1905	Zn/Ba yellow, Hg red, Pb white	1905
At the Edge of the Forest (J. Wayne Stark Gallery, College Station, TX)	1909*	Pb white, Cd yellow	
Central Park (Private collection)	1909–1912	Pb white, Fe red, Cd yellow	Post 1906–1908
Fall Landscape #2 (Private collection)	1899–1906	Pb white, Hg red, Zn yellow, Cu blue	1905–1908
Large Bluebonnet Landscape (Private collection)	1910	Pb and Zn white, Fe red, Sr yellow, Co blue	Post 1906–1908
Summer Afternoon (Private collection)	1905	Org blue, Mn brown	Pre 1908
Bluebonnet on a Texas Landscape (Villa Finale Museum, San Antonio TX)	1910–1913	Pb and Zn white, Fe red, Cd yellow, Co and Sn blue, Mn brown	1910
Study – Lupine (Witte Museum, San Antonio, TX)	1915–1920	Zn white, Pb red, Ba and Sr yellow, Co blue	

*The inclusion of Hg red could suggest an older date, but *Seascape V* supports a 1909 date.

Data availability statement

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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List of abbreviations

As	Arsenic
Ba	Barium
C	Carbon
Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cu	Copper
Fe	Iron
Hg	Mercury
O	Oxygen
Pb	Lead
S	Sulfur
Sr	Strontium
Ti	Titanium
Zn	Zinc
pXRF	Portable X-Ray Fluorescence

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