

USING XRF FOR SEMI-QUANTITATIVE ANALYSIS IN A STUDY OF DELAMINATING PAINT

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ABSTRACT

This paper describes the elemental analysis performed as part of an investigation into the cause of paint delaminating from the ground in some modern paintings. Paintings are very complex systems and there are many variables to consider when determining the cause of any delamination. Composite samples of oil or alkyd paints, over acrylic grounds, were prepared in the lab. Samples were naturally aged for eight years, and some of the samples delaminated. Initial examinations with a hand-held X-ray fluorescence (XRF) unit indicated that zinc could be the common factor in the delaminating samples.

The XRF unit has several modes of operation, and corresponding algorithms to interpret the results; however, none of these modes is appropriate for artists' materials. The resulting percentages were clearly incorrect. There was not enough material in some of the samples and particularly in the actual paintings examined to allow for destructive testing of all the different paints.

More accurate results were required, so where possible, samples were analyzed by the destructive inductively coupled plasma (ICP) method. The XRF spectra of the same samples were integrated and the results compared to the ICP results. Calibration curves for lead and zinc in paint were prepared. The equations from these curves were then used to calculate the percentage of zinc and lead in the other samples and in actual paintings, which could only be analyzed by non-destructive methods because of the limited amount of sample. The accuracy of this method was found to be limited by the thickness of the paint layer.

The results of this project showed that almost all delaminating samples and paintings contained zinc. The severely delaminating paintings contained high percentages of zinc (~16-20%). The zinc and lead calibration curves can now be used to calculate approximate percentages of those elements in any paintings examined by XRF in the future.

INTRODUCTION

Painting in oil or alkyd over acrylic is usually considered a safe practice. In some cases, however, there is severe delamination within just a few months or a few years of painting a work of art. Figure 1 is an example of a painting completely destroyed by delamination. The first image was taken shortly after the painting was completed; the second is a detail showing its current condition, where most of the blue paint has flaked off and some of the green paint is missing as well. A project is currently in progress investigating the cause of such delaminations.

Early on in this process it became clear that zinc in the oil paint could be a significant factor. The presence of zinc can be easily determined with x-ray fluorescence (XRF). The Queen's University art conservation program owns a hand-held XRF, which has been very useful as a non-destructive and very quick method of identifying elements in art objects. For this project identification was not enough, since it was expected that quantities of zinc (or other metals) could be related to the number of samples delaminating or the degree of delamination in an actual painting.



Figure 1: Michael Skalka, 'Colorado Lagoon', Long Beach, CA, Oil and alkyd on canvas, 12''x16'', 2006.
Photo taken immediately after painting. Detail of delamination with ground showing, taken Nov. 2007

Paintings are complex, composite structures with many variables. In order to simplify the investigation, a set of samples prepared in a lab were used. The samples, combinations of 20 oil or alkyd paints over thirteen acrylic grounds, were prepared in 1999 by Marion Mecklenburg of the Smithsonian Institution. After eight years of natural aging some of the samples are delaminating. Since they were all prepared and stored in the same way, all issues relating to technique and environmental conditions can be disregarded. The samples are being examined by many analytical methods to find what the delaminating ones have in common [1].

Zinc is likely to be present in white oil paints, since zinc white (ZnO) is usually added to both titanium white and lead white (flake white) paints in order to improve their handling properties. Zinc, lead and other metals can form metal soaps with fatty acids in the paint [2]. These metal soaps can influence the properties of the paint, for instance it has been shown that lead soaps make the paint stronger [3]. Several theories have been suggested to explain how zinc soaps could cause delamination. These include: strengthening the paint layer too much, or forming a separate layer that prevents adhesion [4].

The hand-held XRF can be operated in different modes, which determine energy levels and filters. Corresponding algorithms convert the spectra to percentages; however, none of the modes will correctly interpret the spectra of artists' materials. This means that the results are qualitative at best. Several of the paints contained lead, which is a heavy metal and provides a large target for x-rays. The algorithm used was apparently not written to accommodate significant amounts of lead, and the interpretation of results was completely incorrect, often resulting in a total of ~300%. While a variety of other elemental analysis techniques were available, they require the destruction of large samples, which could not always be obtained.

This paper describes the use of the destructive inductively coupled plasma (ICP) technique, on a small number of samples, to create calibration curves for the hand-held XRF. The calibration curves were then used to quantify and compare amounts of zinc and lead present in samples analyzed only by XRF.

EXPERIMENTAL

Samples

The 1999 samples were prepared by drawing down parallel strips of acrylic ground on Mylar® (polyethylene terephthalate) and, approximately a month later, strips of the paint were drawn down in the other direction, in a cross-hatch pattern (figure 2a). There are therefore areas of paint alone and areas of uncovered ground, as well as the composite

structures. Several layers of vinyl tape were used to create barriers and a metal scraper was used to draw down the paint in an attempt to make the layers as even as possible. The large sample sheets were eventually cut into smaller samples to facilitate handling (figure 2b).

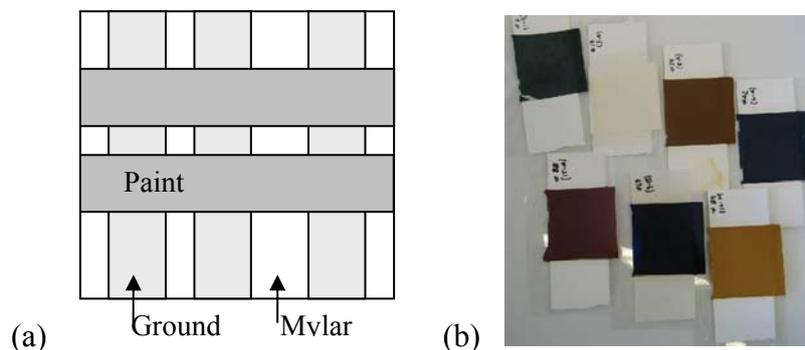


Figure 2: (a) Schematic of composite samples. (b) Various samples after aging.

The samples were combinations of the paints and grounds detailed in table 1. As of March 2008 there are significant numbers of delaminating samples with paints 2, 3 and 4 (titanium white and lead white paints). A few samples with paints 1 and 18 (verdigris with and with-out lead drier) are delaminating as well. None of the samples with other paints are delaminating.

Paints		Grounds	
1	Custom manufactured Verdigris in oil with lead drier (PbO)	A	Aaron Brothers White Gesso
2	W&N*, Titanium White in oil	B	W&N Clear Gesso Base for Acrylics
3	Grumbacher, Flake White in oil	C	W&N Acrylic Gesso Primer
4	W&N, Flake White in oil	D	Utrecht Artists' Acrylic Gesso
5	W&N, Raw Sienna in oil	E	Utrecht Professional Acrylic Gesso
6	Custom manufactured Cobalt blue in oil	F	Liquitex Acrylic Gesso
7	W&N, Titanium White in alkyd	G	Dick Blick Artists' Acrylic Gesso
8	W&N, Flake White in alkyd	H	Grumbacher Artists' Acrylic Gesso
9	Gamblin, Ultramarine blue in oil	P1	Liquitex Basic Titanium White
10	W&N, Raw Sienna in alkyd	P2	Golden Artists Acrylic Titanium white
11	W&N, Cobalt Blue in alkyd	P3	Grumbacher Academy Titanium White
12	W&N, Light Red Oxide in alkyd	P4	Dick Blick Gel Medium
13	W&N, Yellow Ochre in alkyd	P5	Grumbacher Clear Blend Acrylic Medium
14	W&N, Terre Verte in alkyd		
15	Gamblin, Indian Red in oil		
16	Gamblin, Yellow Ochre in oil		
17	Custom manufactured Burnt Sienna in oil		
18	Custom manufactured Verdigris in oil		
19	Gamblin alkyd White		
20	W&N, in alkyd		

* W&N = Winsor Newton

Table 1: Grounds and paints in the 1999 composite samples

In addition, two severely delaminating paintings were examined. The paintings were donated by artists, and are designated by their main colors. Skalka's 'Colorado Lagoon' is 'the blue painting'. It is oil paint over an unidentified ground (not acrylic, alkyd or oil). The second painting is 'the grey/brown painting' and it is alkyd paint over a ground that is probably oil paint. The media were identified by Fourier transform infrared - attenuated total reflectance (FTIR-ATR).

Methods

Two methods of elemental analysis were used, X-ray fluorescence (XRF) and inductively coupled plasma - optical emission spectroscopy (ICP-OES). XRF data was collected with a

handheld, Innov-X systems XT-440L and accompanying Innov-X PC 1.53 software. No sample preparation was needed with this method. Analysis was done in soil (light element matrix) mode and in most cases the test time was 60 seconds. Further analysis was done in Microsoft Excel.

For accurate results the samples need to be homogeneous and ‘infinitely thick’. To test if the paint was thick enough, the area of paint alone on the 1999 samples was carefully separated from the Mylar and small pieces of gold or silver were placed under the paint, to determine if x-rays of various energy are reduced or not. Silver was used as an extreme example since it absorbs at energy levels much higher than anything likely to be found in a paint sample ($K_{\alpha} = 22.16$ keV). Gold was chosen since it absorbs at energy levels similar to lead, which has the highest energy levels of the metals that are of interest in this study ($Pb L_{\alpha} = 10.55$, $L_{\beta} = 12.61$; $Au L_{\alpha} = 9.71$, $L_{\beta} = 11.44$). These tests were done in the analytical mode and test time was usually 60 seconds. Since some of the samples not to be thick enough, additional tests were done with a sample of the same paint inserted between the paint and Mylar, creating a double layer. These tests were done in soil mode, in order to allow comparison with the single layer measurements done on all the samples.

For ICP-OES, samples were taken from paints 1-10 since there were enough of those paints to allow for destructive testing. Samples of approximately 100 mg were dissolved in 2 ml nitric acid and 6 ml hydrochloric acid. The samples were heated overnight (18 hours) until almost dry. Double de-ionized water (25 ml) was mixed in and the solutions were filtered. Analysis was done with a Vista AX CCD simultaneous ICP-AES.

Paints 1-10 were analyzed by XRF as well; the Zn and Pb peaks were integrated in Microsoft Excel. Linear calibration curves were created with the XRF and ICP-OES results. Separate curves were made for zinc in paints with and without lead, to make the results as accurate as possible. The linear fit equations were then used to calculate an estimated quantity of those elements in the paints analyzed only by XRF.

RESULTS

The results of the ICP-OES analysis showed that most of the paints with delaminating samples contained zinc. The verdigris paint obviously contained a high percent of copper, but also some lead, since litharge, PbO , was added to the paint as a drier. Since two of the delaminating paints were lead-white paints, the elements reported in table 2 are Pb, Zn and Cu. The quantities reported are accurate within approximately 50 ppm.

Sample	Zn (ppm)	Pb (ppm)	Cu (ppm)
1 Verdigris in oil	13.23	2446.52	272786
2 Titanium White in oil	63488.7	312.21	25.65
3 Flake White in oil	34785.5	578680	9.45
4 Flake White in oil	124263	485923	17.37
5 Raw Sienna in oil	556.42	61.92	231.84
6 Cobalt Blue in oil	35.14	78.24	21.56
7 Titanium White in alkyd	593.28	13.52	19.94
8 Flake White in alkyd	172.05	636407	19
9 Ultramarine Blue in oil	58.25	6.69	18.4
10 Raw Sienna in alkyd	121.74	21.48	134.71

Table 2: ICP-AES results for zinc, lead, and copper

Figure 3 shows an example of an XRF spectrum of paint 2; the area under the zinc peak was integrated. With the ICP-OES and integrated XRF results, calibration curves could be made. The calibration curves for lead and zinc are shown in figures 4 and 5 respectively.

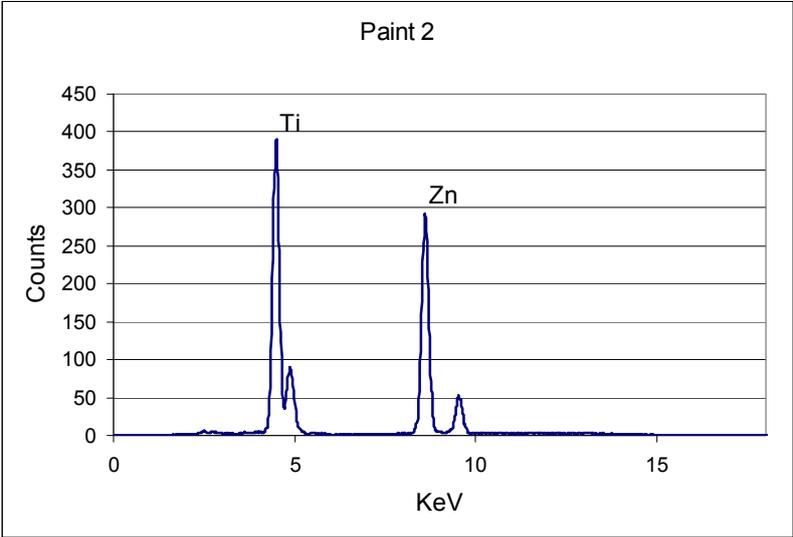


Figure 3: XRF spectrum of paint, Titanium White in oil.

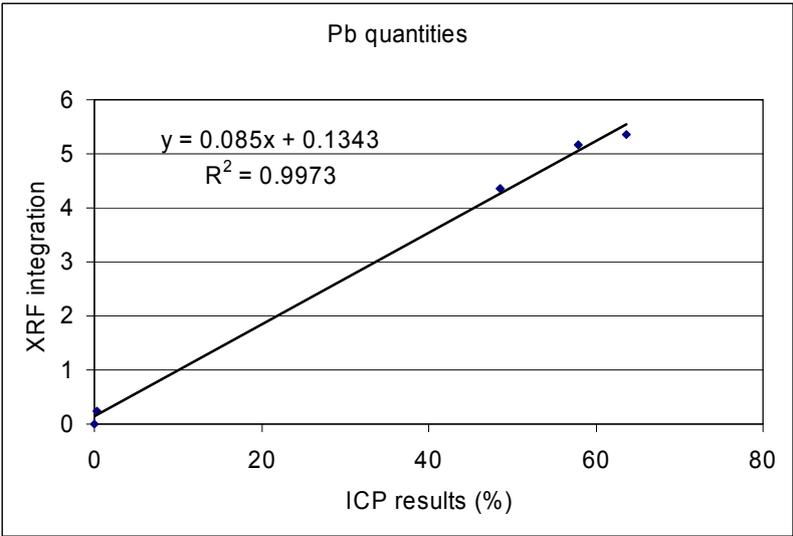


Figure 4: Calibration curve comparing lead quantities by XRF and ICP.

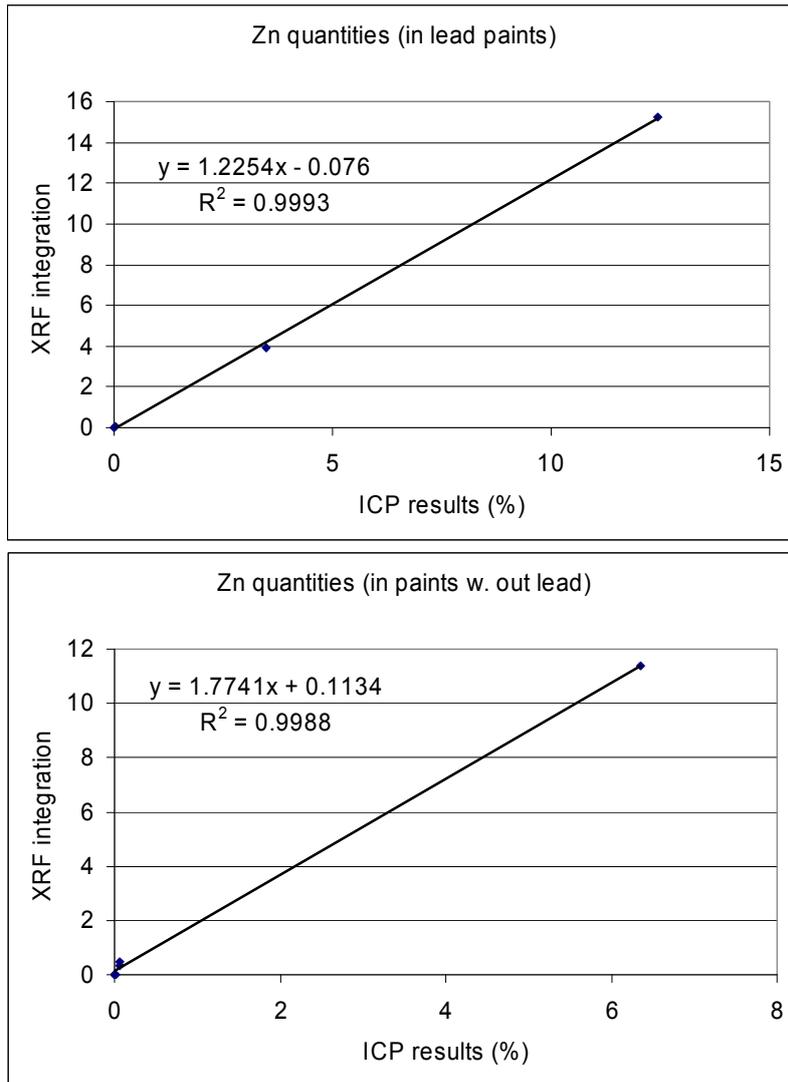


Figure 5: Calibration curves comparing zinc quantities by XRF and ICP.

Based on the calibration curves, the XRF results obtained from the paintings and from paints 11-20 in the 1999 samples were converted to approximate quantities. The results are summarized in table 3.

Sample		Zn (ppm)	Pb (ppm)	Cu (ppm)
Blue paint from 'blue painting'		~190000	~43000	none
Green paint from 'blue painting'		~70000	~40000	none
Ground from 'blue painting'		~110000	~58000	none
Paint from 'grey/brown painting'		~160000	~15000	a little
Ground from 'grey/brown painting'		~210000	~26000	none
11	Cobalt Blue in alkyd	~100	none	none
12	Light Red Oxide in alkyd	none	none	none
13	Yellow Ochre in alkyd	none	none	none
14	Terre Verte in alkyd	none	none	trace
15	Indian Red in oil	none	none	none
16	Yellow Ochre in oil	none	none	none
17	Burnt Sienna in oil	~1000	trace	trace
18	Verdigris in oil	none	none	a lot
19	white alkyd (TiO ₂ + ZnO)	~45000	none	none
20	Burnt Umber in alkyd	~1000	trace	trace

Table 3: Elemental analysis of delaminating paintings

Several paints were measured with pieces of gold or silver placed behind the paint. Silver always showed on the spectra, indicating that the paint film is not thick enough to completely reduce 22 keV x-rays. Gold did not show in spectra collected from lead white paints, but did show up when placed behind titanium white paint, raw sienna paint (figure 6), and very faintly behind verdigris paint. Gold peaks were much larger in the alkyd titanium white than in the oil titanium white.

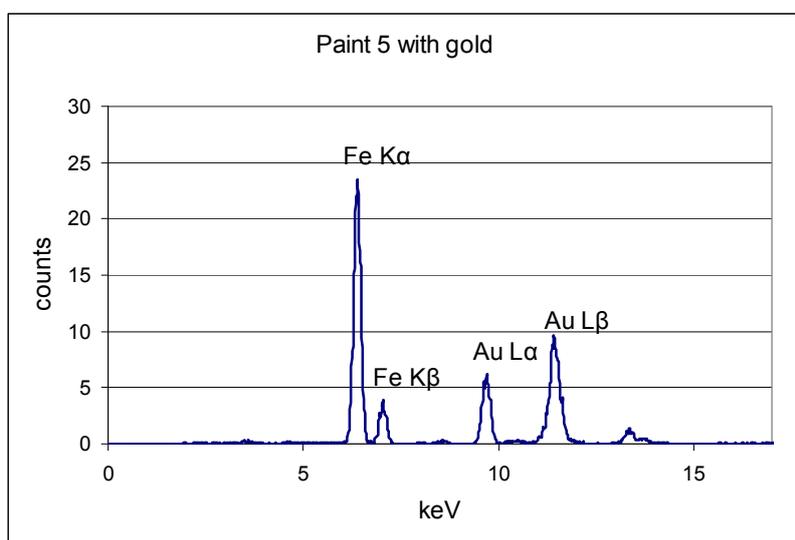


Figure 6: XRF spectrum of raw sienna oil paint with a piece of gold behind it.

With the titanium white paint (2) and raw sienna paint (5), it was possible to insert another sample between the paint and Mylar. As expected, there were differences in the spectrum of a single layer of paint and a double layer (figure 7). The zinc peak in the titanium white double layer was 5% larger than in a single layer. In the raw sienna double layer the very small zinc peak was almost 20% larger than in a single layer. For the verdigris paint (1), it wasn't

possible to test a double layer of paint, so the magnitude of error was estimated from the test with gold behind, by adding the gold L_{β} peak to the lead L_{α} peak. The gold added ~30%.

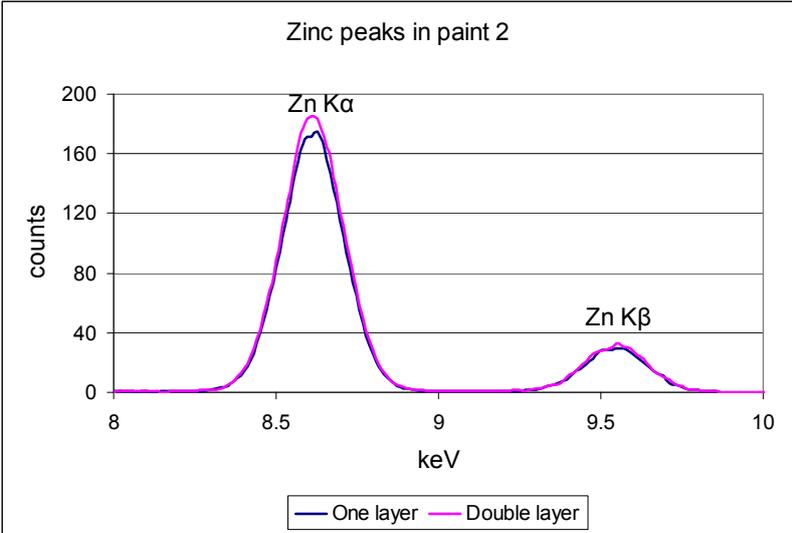


Figure 7: XRF spectra (from 8 to 10 keV) of single and double layers of titanium white oil paint.

DISCUSSION

When the thickness of paints was tested, it was discovered that some of the paints are not thick enough to be considered infinitely thick. The thickness (t) required can be calculated for specific materials, provided their density (ρ) and mass attenuation coefficient (μ/ρ) are known. This information is available on the NIST website [5] for pure elements. Since a dry film of titanium white oil paint is mostly TiO_2 , it is interesting to check the thickness required for Ti (figure 7). The curve was created using the equation: $\chi = (\mu/\rho)^{-1} \ln(I_0/I)$ where χ is the mass thickness $\chi = \rho t$, I_0 is the initial intensity and I is the final intensity. The K_{α} line for titanium is at 4.51 keV, which means that for pure Ti, a thickness of 0.003 cm or higher could be considered infinitely thick. In a similar fashion it can be determined that zinc needs to be 0.007 cm thick, lead approximately 0.0035 cm thick and copper 0.01 cm thick. If the sample is not thick enough, x-rays make it through to the gold placed behind the paint layer. For gold ($L_{\alpha} = 9.71$) behind titanium, the graph in figure 8 indicates that a thickness of at least 0.009 cm would be necessary.

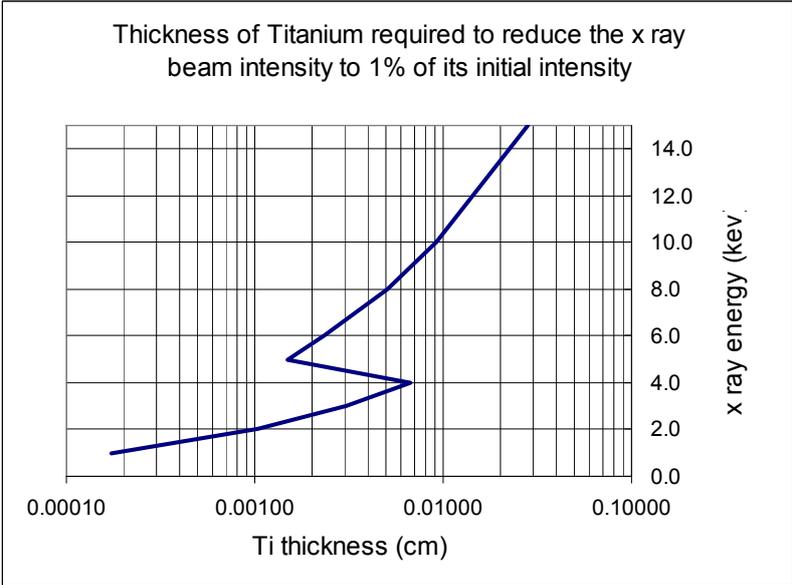


Figure 8: Thickness of titanium vs. x-ray energy

The thickness of the titanium white paint layer was measured with calipers and its average thickness is 0.03 cm; however, since it is not only made of metals, but rather a less dense material, the x-rays are not reduced entirely. This results in an XRF spectrum showing gold in addition to the zinc and titanium present in the paint film, similar to the spectrum obtained when a piece of gold was placed behind a raw sienna paint layer (figure 6).

The thickness testing indicates that the XRF results were often lower than they would have been in a thicker sample of the same composition. When the sample being measured by XRF is not infinitely thick, any variations in thickness influence the results. The samples were prepared in a method that was meant to produce samples of even thickness; however, there are slight variations. This means that the results aren't uniformly lower, and so cannot be corrected easily; therefore, the integrated value measured from the titanium white paint has an estimated error of $\pm 5\%$. Estimated errors are based on the assumption that the double layers of paint tested were infinitely thick. When only trace amounts of zinc or lead were present, as in the raw sienna and verdigris paints, the error can be much larger and is estimated at $\pm 20\%$ for zinc and $\pm 30\%$ for lead; however, that does not change the order of magnitude of the results. When large amounts of lead were present, the paint layer is essentially 'infinitely thick', so the results are quite accurate.

The margin of error for the results in table 3 is fairly large, in particular for the measurements taken from actual painting, where the paint can be very thin and uneven. For the purposes of this project however, these inaccurate results are perfectly adequate, since the differences in zinc and lead quantities between delaminating and non-delaminating samples were very large. For example, in the 'blue painting', the zinc in the severely delaminated blue paint was estimated at 19% and about 7% in the slightly delaminated green paint. Since these are significant quantities and not trace amounts, the margin of error is not very large. Even if those results are wrong by 5%, as in the titanium white paint discussed above, the difference would still be significant. Since zinc is a heavier element than titanium and there is lead in the paints as well, the paint is probably closer to an infinitely thick layer, making the results more accurate.

The elemental analysis indicated a strong correlation between the presence of zinc in the paint or ground and the presence of delaminations. If there was lead in addition to zinc in the paint, the problem was exacerbated. In both the severely delaminating paintings, there were high levels of zinc and some lead in both the paint and the ground. In the 1999 samples, more samples with lead white paints (3 & 4) are delaminating than samples with titanium white paint (2), which contains almost twice the zinc as paint 3.

The fact that metals from the pigments had formed metal soaps was confirmed with FTIR-ATR and those results are detailed elsewhere [6]. It was seen that all delaminating samples contained metal soaps and well-adhered samples did not. The mechanism by which metal-soaps, and specifically zinc soaps, cause delamination is, at this point, still unknown. Other factors, such as the roughness of the ground, also influence adhesion; however, zinc and lead in the form of metal soaps seem to be the main issue and hand-held XRF allows us to check for those metals non-destructively.

CONCLUSIONS

In conclusion, using hand-held XRF to measure the percent of metals in paints was not as straight-forward a process as hoped for at the beginning of this project; however, it did work. By performing destructive ICP testing on a minimal number of samples, it was possible to create calibration curves. Thus, semi-quantitative data was obtained for a larger number of samples which could be measured only with the non-destructive XRF. The accuracy of the XRF results was limited because the samples were too thin and not entirely uniform in thickness. In this case it was determined that more accurate results were not required.

The results clearly showed that zinc plays an important role in the delamination of paints. Lead appears to cause even more severe delaminations when it is combined with zinc. Now a quick XRF test can be used to check for the presence of zinc and lead to determine if a painting is at risk for delamination.

ACKNOWLEDGMENTS

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END NOTES

1. More details on the other methods used and results are in: Y. Maor and A Murray, *Materials Issues in Art and Archeology VIII* (in press), and Y. Maor, master's thesis, Queen's University (in preparation).
2. L. Robinet and M. C. Corbeil, *Studies in Conservation* 48, 23-40 (2003).
3. A. Stewart, *Official Digest, Fed. Paint & Varnish Prod. Clubs* 311, 1100–1113 (1950).
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K. J. van den Berg (personnel communication) 2008.
5. <http://physics.nist.gov/PhysRefData/XrayMassCoef/cover.html>
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