SA ПУБЛИКУЕТ ТЕКСТ СТАТЬИ «АНАЛИЗ ЗАКРЕПИТЕЛЕЙ, СИККАТИВОВ И ЛЯПИС-ЛАЗУРИ С ИСПОЛЬЗОВАНИЕМ РЕНТГЕНОВСКОЙ ФЛУОРЕСЦЕНТНОЙ СПЕКТРОМЕТРИИ: СРАВНИТЕЛЬНОЕ ИССЛЕДОВАНИЕ С ИСПОЛЬЗОВАНИЕМ ВОСПРОИЗВЕДЕННЫХ ОБРАЗЦОВ КРАСКИ И ПРИМЕРЫ ИССЛЕДОВАТЕЛЬСКИХ РАБОТ». ПЕРЕВОД ДАННОЙ СТАТЬИ НА РУССКИЙ ЯЗЫК РАЗМЕЩЕН В ОТКРЫТОМ ДОСТУПЕ НА САЙТЕ SA: HTTP://SECART.ELPUB.RU/. АВТОРЫ ИССЛЕДОВАНИЯ – БРАЙАН БААДЕ, КРИСТИН ДЕ ГЕТАЛЬДИ И АЛИССА РИНА (ДЕЛАВЭРСКИЙ УНИВЕРСИТЕТ, США: WWW.UDEL.EDU). ТЕКСТ ПУБЛИКУЕТСЯ В АВТОРСКОЙ ВЕРСИИ

ANALYSIS OF MORDANTS, DRIERS, AND LAPIS LAZULI USING X-RAY FLUORESCENCE: COMPARATIVE RESEARCH USING RECONSTRUCTED PAINT SAMPLES AND CASE STUDIES

Brian Baade[1], **Dr. Kristin deGhetaldi**[2], **and Alyssa Rina**[3]

[1]Paintings Conservator, Assistant Professor, Department of Art Conservation, University of Delaware, Newark, USA; [2] Paintings Conservator, Department of Art Conservation, University of Delaware; deGhetaldi Fine Art Restoration, LLC, Newark, USA; [3] Independent researcher, Graduate Fellow (Class of 2023), Winterthur/University of Delaware Program in Art Conservation, USA

Abstract:
Changes in the formulation of pigments and paint binders and the presence of additives used in the history of painting can complicate the interpretation of analytical data and may influence the characterization of the materials used in artworks. The limitations of the common analytical tools used to identify potential paint components including metallic driers, pigments, and the inorganic substrates of lake colors may also make analysis more difficult. X-Ray Fluorescence (XRF) spectroscopy is a common non-destructive technique used to collect inorganic elemental information from artworks. Advancements in XRF technology now permit the gathering of data from multi-layered paint systems and scanning technology can help characterize pigments across the entire surface of an artwork. These tools require an even greater understanding of the potential materials in an artwork to avoid misinterpretation of the data. The authors tested XRF's ability to characterize lead, manganese, and cobalt driers. The presence of metallic driers could have an impact on the interpretation of the inorganic components in paint films. Lake pigment substrates often contain aluminum, tin, and calcium salts. The detection of these ions was also studied. Finally, the XRF detection of aluminum in lapis lazuli samples was assessed. These three groups of materials were also mixed with driers and/or other pigments to determine whether the presence of additional metal ions inhibited the detection of the characteristic elements. The authors used a Bruker ArtTax Micro XRF and a handheld Bruker Tracer III-SD XRF unit with and without a vacuum or helium purge for these experiments.

Keywords:
Artwork analysis; XRF; Paint driers; Lake Pigments; Lapis lazuli; Lead white; Megilp; Art materials history

Corresponding Author Contact Information: Baade, B.; 18 East Main St., Old College room 302, Newark, DE 19716, USA
E-mail: bbaade@udel.edu
Phone 302 897-8125

Introduction

Changes in the formulation of pigments and paint binders throughout the history of Western easel painting can impede the interpretation of analytical data and the characterization of materials in artworks. Paint may contain additives that should be considered when interpreting results obtained during both inorganic and organic analysis. Inorganic analysis of paint is further complicated by the incomplete understanding of the precise limitations of the common analytical tools used for the detection and identification of potential additives, especially metallic driers, pigments, and the substrates of organic lake colors. X-Ray Fluorescence (XRF) spectroscopy is a non-destructive technique that is often used to collect elemental information associated with inorganic materials in artworks. In previous years, elemental data of complex painted surfaces could only be obtained from cross-sections, which required destructive sampling. Recent advancements in XRF technology can now permit the gathering of elemental information in multi-layered paint systems and allow for the characterization of pigments across the entire surface of an artwork with scanning technology (Dik et al., 2008; Alfeld et al., 2012; Alfeld et al., 2013). Powerful tools like these require an even greater understanding of the materials potentially present in an artwork in order to avoid misinterpretation of the data.

While many publications on the recent developments in XRF technology have focused on pigment analysis, the successful detection and characterization of inorganic components associated with paint additives is a topic that requires further study. Such information should be considered a prerequisite when attempting to identify inorganic pigments in painted artworks. If metallic driers or siccatives are detectable in the concentrations traditionally used in artistic practice, this could have a major impact on the interpretation and characterization of the inorganic components in paint films. The incorporation of driers could easily affect the characterization of pigmented layers as they share similar elements with certain pigments. Lake pigment substrates are often based on aluminum salts but can also contain tin and calcium (Kirby et al. 2014). In addition, lead, copper, and iron are all components listed in historical lake recipes (Riffault et al. 1874). The interpretation of XRF data could be greatly improved by a better understanding of the possible influence of these components. Therefore, the presence of the elements associated with lakes could confuse or complicate XRF analysis if their presence is not considered. Additionally, the concentration of the various pigments, siccatives, and mordants can vary throughout the paint layers and these could greatly influence the interpretation of data, particularly if the analyst is attempting to accurately detect and characterize paint mixtures and layering stratigraphy. Finally, due to inherent differences in instrumentation (e.g. detectors, spot size, architecture, etc.) not all XRF systems are equally effective at detecting low-molecular weight elements associated with certain pigments. This aspect of XRF instrumentation may lead to mischaracterization of painted artworks if spectra from different instruments are interpreted using the same criteria. One aim of this study is to explore some of the discrepancies that might be encountered when analyzing the same set of samples with different instrumental models.

The first portion of this study documents the XRF analysis of metallic driers, including lead, manganese, and cobalt ions. Most of the driers were created from historically representative recipes and concentrations including leaded oil, lead-manganese oil, lead-containing megilp paint medium, and gumption paint medium containing lead acetate. Due to the difficulty of producing a representative reconstruction of cobalt napthenate, commercially available cobalt drier was also analyzed. Unpigmented and pigmented samples of these driers/mediums were analyzed and compared to standards to determine detectability. Calibration curves were created using thin film standards (cited as µg/cm2) on loan from the Getty Conservation Institute in order to determine the concentrations or certain elements detected in the reconstructed paint samples. All samples were analyzed using a Bruker ARTAX Micro XRF unit as well as a handheld Bruker Tracer III-SD XRF spectrometer.

The second portion of this study compares results obtained from the XRF analysis of oil paints containing red lakes made with aluminum, tin, and calcium-aluminum substrates. The reconstructed lakes were also mixed with metallic driers and mediums to determine whether their presence inhibited the characterization of the lake substrate. Analysis was performed using XRF units fitted with a vacuum or helium purge, depending upon the instrument, in order to allow for the characterization of elements lighter than potassium.

The final portion of this study evaluated various samples containing lapis lazuli pigment. Paints made from two forms of true lapis lazuli pigment (a natural ultramarine refined according to Renaissance methods and a lapis pigment made from simply grinding the raw stone) were analyzed using the two XRF units. As with other samples, the lapis pigments were mixed with driers to see whether the presence of additional metal ions inhibited the detection of aluminum.

Analytical Methods

All samples of driers and paints containing driers, red lake oil paints, and Lapis Lazuli oil paints were created according to traditional practice and allowed to dry for several weeks. Samples were then analyzed using a Bruker ARTAX micro XRF unit, an open architecture system that uses a rhodium tube with an element detection range of potassium (K) to Uranium (U). Polycapillary optics allow for a small spot size, approximately 70–100 microns. All spectra were interpreted using the Intax version 4.5.18.1 software. The spectrum was captured with and without a helium purge using the following parameters: 600µA current, 50kV voltage, 300 seconds live time irradiation. Additional analyses were performed with the handheld Bruker Tracer III-SD XRF spectrometer equipped with a rhodium tube and interpreted within the PXRF1 software (spot size approximately 1 cm x 0.5 cm). Lower Z elements were analyzed under vacuum with no filter, using the parameters of 15kV high voltage, 55µA anode current, 100 seconds live time irradiation. Higher Z elements were analyzed using a Ti/Al 25µm/305µm filter using the parameter of 40kV high voltage, 10µA anode current, 300 seconds live time irradiation. These particular parameters were chosen as they were highly recommended by conservation scientists who specialize in XRF analysis. It should also be noted that since the time of this study, Bruker has manufactured additional handheld models that have improved detection capabilities.

Thin film standards provided by the Getty Conservation Institute, were used to create calibration curves by calculating the net area under the primary peaks associated with various

DOI: 10.51236/2618-7140-2020-3-4-84-95

elements. Any contributing elements from the Mylar substrate were subtracted from the spectra. The obtained values were used to estimate the concentration (microgram per cm squared) of the detected elements in the paint samples. Both instruments were positioned approximately 3–4 mm away (Z axis) from the surface of the reconstructed paint samples and artworks during data collection.

DRIERS AND SICCATIVES

History of use and types of driers

Inorganic salts and solutions can be added to drying oils to catalyze oxidation reactions and quicken the drying time associated with these mediums. The technology associated with driers or siccatives has been known since the adoption of oil painting and the use of oil-containing varnishes (Elm 1934). The earliest reference to the use of driers in combination with oil dates to the second and third centuries and can be located in written accounts attributed to the Greek physician Aelius Galenus known as Galen (Eastlake 2001). Driers were also used in the preparation of traditional oil varnishes, varnishes that typically contained a drying oil (e.g. linseed oil, walnut oil) and natural resins such as sandarac, mastic, and rosin (Phenix and Townsend 2012). The first known oil varnish recipe is detailed in the *Mappae Clavicula*, a compilation of various manuscripts and recipes (including the *Lucca Manuscript*) that date as early as the eighth and ninth centuries, although the central core of the manuscript may date even earlier (Smith and Hawthorne 1974). Early varnish recipes involved heating natural resins until they could be effectively combined with drying oils at extremely high temperatures. Oil varnishes are not to be confused with spirit varnishes (when a natural resin is directly dissolved in an organic solvent), materials that appear to have been adopted for artistic practice much later (Phenix and Townsend 2012). It is likely that early oil varnishes contained driers to help speed the oxidation processes and hence the dry time associated with these surface coatings.

Some of the earliest driers were lead-containing pigments (e.g. red lead, lead white). Lead white is the most important white used in easel painting at least until the mid-20th century, and the history and properties of lead white are well covered in the National Gallery of Art's *Pigment Handbooks* (Gettens et al. 1993). Lead white alone, however, has been shown to only minimally increase the oxidation of drying oils (Boughton 1916). Impurities in lead white, such as lead acetate and litharge, probably account for the perceived catalytic effect of lead white pigment (Tumosa and Mecklenburg 2005). Lead salts can also be dissolved into hot oil to create leaded oil. Leaded oil will also increase oxidation but, unlike the addition of powdered lead pigments, it does so without adding turbidity to an oil varnish, while substantially speeding up the drying process. This quality would also allow the artist to speed up the drying of notoriously slow drying oil paints, like those containing red lakes or carbon black, without greatly affecting the color. While the use of leaded oil driers was likely common in historical practice, we have few specific ancient recipes for their production. Additionally, the ingredients in oil varnishes likely changed over centuries, and the proportions of each ingredient cannot be precisely known.

Lead and manganese are important elements in pigments, mediums, and driers. The ubiquity of lead and manganese pigments in traditional paintings has made it difficult to detect the addition of driers in early varnishes and paints. Work done by the National Gallery; London does suggest the use of red lead as a siccative in an oil containing varnish on a late fourteenth-century panel by Jacopo di Cione (Bomford et al. 1989). The drying properties of manganese were realized quite early, as this element has been found to have a much stronger catalytic effect on the auto-oxidation of oil paints than lead (Steele 1924). Commonly used umber pigments derive their color from a combination of mixed phases of iron oxide and manganese dioxide (Helwig 2007). It is not known how early manganese was used to create a siccative oil, but recipes dating to the mid-eighteenth century include the addition of lead white, lead acetate, raw umber and other materials. Such oils are referred to as "coarser drying oils" to differentiate them from lighter colored, carefully cooked leaded oils (Carlyle 2001). Many recipes for driers and lead/manganese-containing oil mediums can be traced to eighteenth and nineteenth centuries (Carlyle 2001). Megilp mediums (containing leaded oil and mastic resin) were developed as early as the eighteenth century while recipes for gumption (an "improved" medium containing lead acetate and mastic resin) were included in a popular reference published in 1828 (Carlyle 2001). The twentieth-century restorer and author, Jacques Maroger, spent a large portion of his career attempting to rediscover techniques used by Old Master painters. He eventually postulated that painters, such as Peter Paul Rubens, used a medium similar to megilp, although no scientific evidence was published to support this conclusion. Since the publication of Maroger's book, *The Secret Formulas and Techniques of the Masters*, in 1948, there have been selected circles of artists who continue to use megilp, despite the unfortunate ramifications associated with the long-term preservation of these sensitive paintings (Maroger 1948; Mayer and Myer 2002).

The drying properties of cobalt salts were likely realized with the introduction of the pigment smalt around the fifteenth century (Lutzenberger et al. 2010; White and Kirby 1994). Ralph Mayer mentions an 1852 Belgian reference to cobalt cooked into an oil to create cobalt linolate driers (Mayer 1957). Riffault mentions the use of cobalt driers in a manual dated to 1874 (Riffault et al. 1874). Cobalt lineolate was later superseded by other cobalt solutions, particularly cobalt napthenate. Commercial cobalt driers available today may also contain additional metallic salts to allow for even drying throughout the paint layers, although such formulations were beyond the scope of the outlined experiment (Bellettiere and Mahoney 1987).

The XRF detection of inorganic paint components can be complicated by the uneven distribution of binding media and pigments within and across the surface of a painting. These variances are contingent upon the intended effects and sometimes idiosyncratic techniques used by the artist. Recent analysis performed on several works by Leonardo da Vinci (focusing on his *sfumato* technique) has suggested that XRF analysis can be used to determine the relative thickness of each paint layer, generating non-destructive, virtual cross-sections of a given painting based on the distribution and appearance of peaks associated with lead carbonate (De Viguerie et al. 2010). However, the study attributed all lead peaks to the lead white pigment and did not account for the possible presence of lead driers, Leonardo is known to have experimented with lead driers based on his own writings (Ritcher 1883). Further research is needed to explore the potential impact that leaded driers might have when calculating the theoretical thickness of paint layers.

Preparation of Driers and Siccatives

The following driers were selected for analysis: leaded drying oil (Pb), coarse drying oil (Pb, Mn), gumption (Pb), meglip (Pb), and a commercial cobalt napthenate drier (Co). Paints and driers were applied to a Mylar substrate for analysis. Recipes for those that were created in-house were collected or extrapolated from historical sources. The Leaded drying oil contained 30g litharge (lead II oxide) and 200ml cold-pressed linseed oil. The mixture was slowly heated to 230°C until the lead had dissolved, and the solution was clear. The mixture was allowed to cool and then allowed to settle for several weeks. After the unincorporated material had settled out of solution, the final product was decanted and collected. Coarse drying oil was made by heating a mixture of 212ml cold-pressed linseed oil, 6.4g gum Arabic, 25.5g litharge, 6.4g lead acetate, 12.75g zinc sulfate, and 6.4g of raw umber. The mixture was heated at 250°C and allowed to settle before decanting (Carlyle 2001). Gumption was made by grinding 1.3g mastic resin with 1.3g lead (IV) acetate followed by the addition of 1.63g linseed oil. The megilp used for this study was prepared by mixing a 1:1 ratio of leaded drying oil (see above) with heavy mastic varnish (1 part mastic resin by weight to two parts double distilled gum turpentine by volume) (Carlyle 2001). The cobalt drier used was a commercially produced cobalt (II) napthenate sold by Grumbacher.

Analysis of Driers and Siccatives

Lead was detected in both pigmented and unpigmented films. Similar results were obtained using both the ARTAX and handheld Tracer III-SD XRF systems, although detection ranges appeared to be far greater using the ARTAX unit (see Table 1). It is important to note that the approximate concentrations listed in Table 1 are the reported values (after calibration has been carried out) and likely not the actual values; this is particularly evident in the case of the handheld unit which is known to possess lower detection limits as compared to the ARTAX. The highest amount of lead was detected in the gumption samples, with megilp samples containing the lowest amount. Analysis of the coarse drying oil samples did detect the small amount of manganese. Interestingly, no zinc was detected using either instrument, suggesting that the zinc

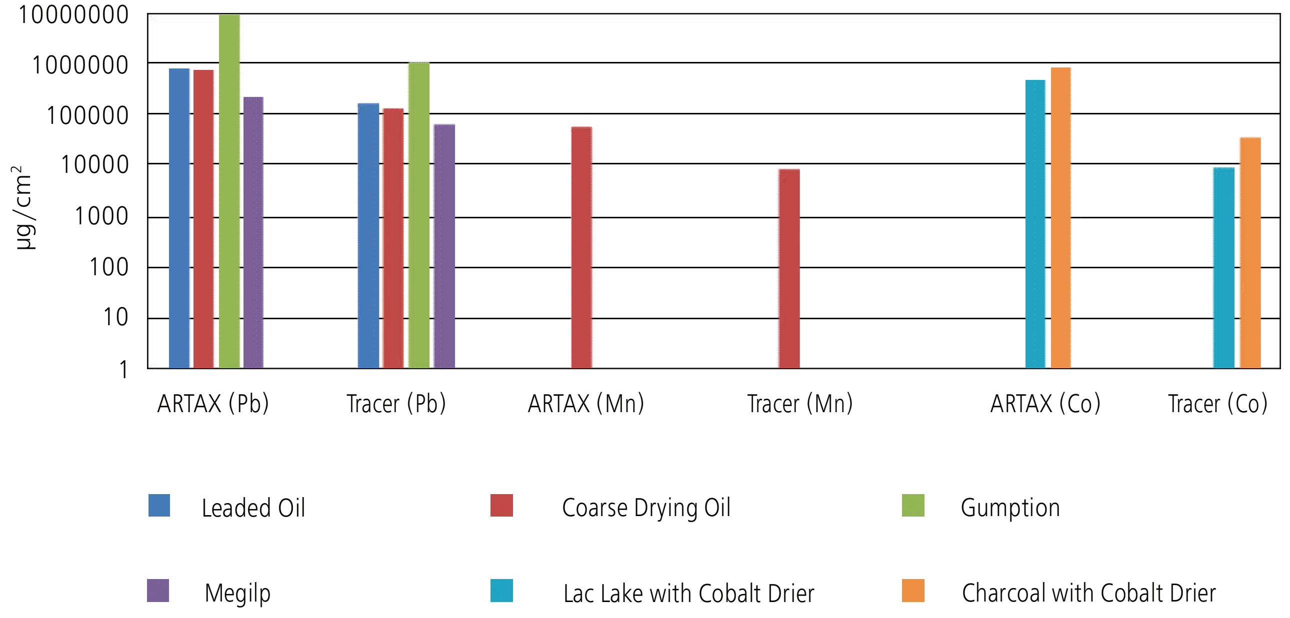

Table 1

sulphate was not successfully incorporated into the coarse drying oil. Cobalt drier was added directly to the oil paint and not through an additional medium or diluent in order to allow for more precise measurements. The drier was thoroughly mixed into each of the paints in the ratio of one drop to a teaspoonful (approximately 5 ml) of oil paint. Cobalt was readily detected in all samples containing cobalt drier. Levels of cobalt were recorded at 430,225µg/cm^2 using the Bruker ARTAX Micro XRF unit in the paints sample containing cobalt drier mixed with lac lake and linseed oil, whereas the handheld Bruker Tracer III-SD XRF spectrometer detected 8,764µg/cm^2. The paint containing cobalt drier mixed with charcoal and linseed oil yielded results of 714,255µg/cm^2 with the ARTAX unit and 28,379µg/cm^2 with the handheld unit. The ARTAX generated greater detection limits associated with calcium, aluminum, and sulfur when these elements were present in the pigmented films as compared to the handheld unit. These can be attributed to the pigment present and not the drier as the same elements were not found in spectra collected from the unpigmented oil film. These results suggest that driers can be readily detected using XRF. Interpretation of XRF data of painted artworks should therefore consider the potential presence of these materials, especially as new technologies like Macro XRF scanning (MA-XRF) become more frequently applied to the non-destructive analysis of easel paintings and painted surfaces (Dik et al., 2008; Alfeld et al., 2012; Alfeld et al., 2013). The presence of lead, manganese, and cobalt should not automatically be assigned to the presence of pigments that contain these elements.

Case Study: XRF Analysis of a painting by Robert Minor

XRF analysis was carried out on Great Silas at Night (1890) and *Souvenir of Italy* (1890s) (Figure 1) by the Barbizon painter, Robert Minor. XRF analysis revealed the presence of cobalt throughout the surface of the painting, however SEM-EDS analysis could not detect any co-localization of cobalt with pigment particles (particularly blue, violet, or green pigments) or aggregates, although cobalt was found to be present in the EDS spectrum. The presence of cobalt drier was initially discounted as the date of the painting preceded that of the common date typically associated with the use of cobalt driers. However, Riffault et al. (translated for the American audience in 1874) suggests that a cobalt drier could indeed have been used by Minor, either as an additive or as an ingredient in a commercially produced oil paint (Mayer 1956; Riffault et al. 1874). This case study suggest that further research is needed for the systematic detection and characterization of driers in oil paintings.

DETECTION OF LAKE PIGMENTS AND THEIR ASSOCIATED INORGANIC SUBSTRATES

History of Use and Types of Lake Substrates

As can be gleaned from reading Hofenk de Graaff and other texts, natural dyes can be extracted from insects, sea snails, lichens, trees, and plants. Red and yellow natural dyes are the most commonly encountered organic pigments found in traditional easel paintings, however only red dyes were analyzed in this experiment, which included shellac, cochineal, and madder root. Cochineal insects (*Dactylopius coccus*) are wingless insects native to Central and South America. American cochineal contains only carminic acid as a coloring component, unlike European variants (Kirby and White 1996). Stick lac or raw unrefined shellac is a resin produced by the female lac insect (*Laccifer lacca or Coccus lacca*), which is native to Southeast Asia plants. The insect secretes the resin as a protective coating while boring into the branch (Hofenk de Graaff 2005). The unrefined form of this resin, called sticklac, contains a red dye composed of laccaic acid. The dye was generally removed from the resin prior to the production of more refined forms of shellac (Harley 1982). The roots of the common madder plant, *Rubia tinctorum*, is composed of several types of red anthraquinone dyes, including purpurin, pseudo-purpurin, and alizarin, with the latter generally regarded as the most lightfast (Kirby et al. 2014; Schweppe and Winter 1997).

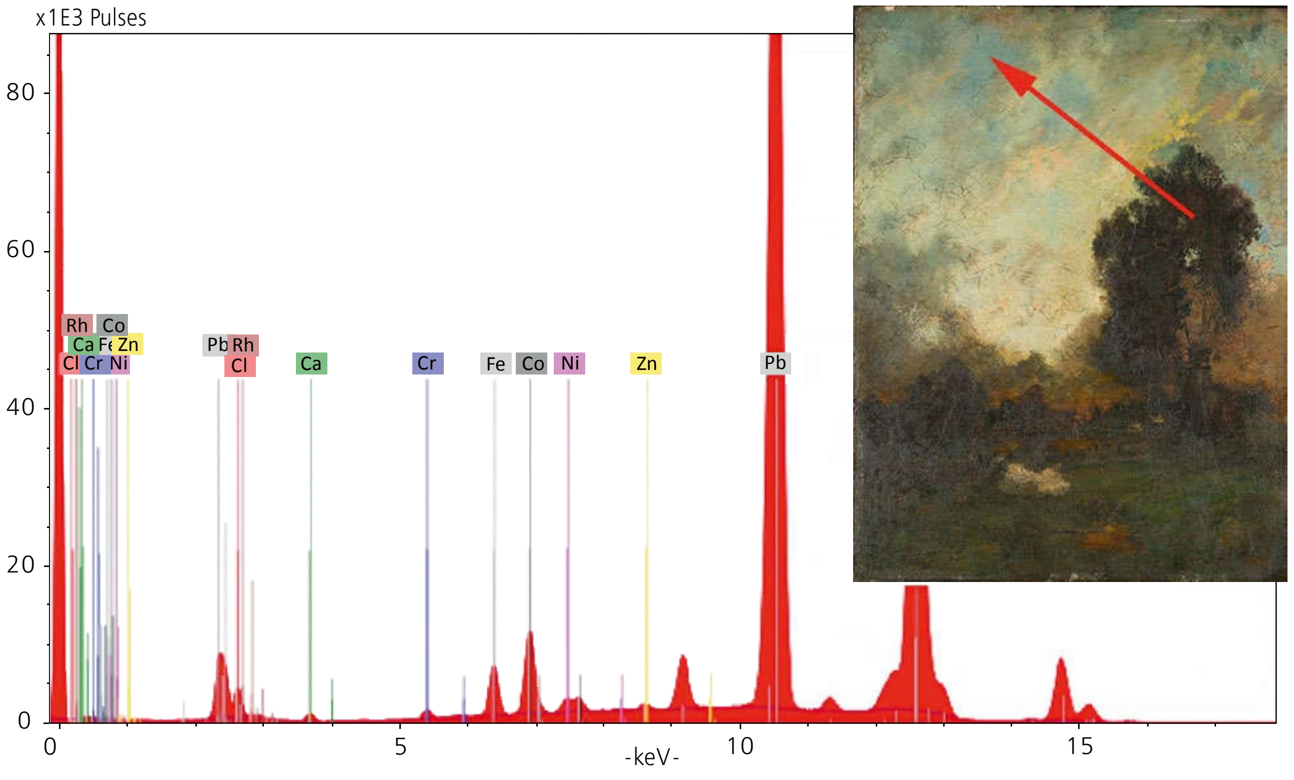

Figure 1

With few exceptions, organic dyes cannot be used directly as colorants in paint. They are generally water-soluble and need to be complexed with or absorbed onto an inert inorganic material. This process is similar to, and likely derived from, the mordanting of dyes on textiles. An early traditional substrate used for this purpose is amorphous hydrated alumina. A common method used up until the late eighteenth century involved the use of a hot aqueous, alkali solution to extract the dye (either from dyed fabric clippings or directly from the raw dyestuff). Traditionally, the alkaline solution consisted of potassium carbonate or potassium hydroxide, but later sodium carbonate became more commonly used, as it was readily available and relatively cheap. The resultant colored liquid would then be filtered to remove the residual dyestuff from the dye. Alum (aluminum potassium sulfate) was then added to precipitate the dye onto the aluminum hydrate, creating a water-insoluble pigment. Once the pigment had settled, any uncomplexed dye was rinsed away and the remaining lake pigment was dried for use. The name lake is derived from the word lac which in turn originates from the term shellac, an important source of red dye throughout the history of easel painting (Kirby et al. 2014).

Early lakes were also made by dissolving scraps of fabric containing the dye rather than extracting it directly from the natural dyestuff. Dyes obtained by dissolving wool to release the color will also contain sulfur from the animal hair. By the late eighteenth century, lakes were often made using a reverse process whereby the dye was first extracted in hot water, filtered to remove the dyestuff, and mixed with alum before being precipitated with the alkaline salt. Lakes made in this manner will retain the sulfate groups from the alum which will subsequently become incorporated into the alumina substrate as it is precipitated. While aluminum is a common inorganic element associated with red lakes, other elements from the natural dyestuff or its growing environment may also be detected. Jo Kirby has described how madder roots (which are used to make madder lakes) can preferentially uptake calcium from the surrounding soil (Kirby et al. 2005). Recipes for yellow and red lakes made from brazilwood often called for the addition of calcium carbonate derived from chalk or eggshells to create a more opaque pigment (the substrate of these pigments can therefore contain both aluminum and calcium). The potential presence of a calcium-containing substrate may be easy to overlook, particularly when an easel painting is analyzed using only XRF since calcium may be present as a filler and/or in underlying ground layers (Bonizzoni et al. 2007). Tin salts (usually in the form of $SnCl_4$) were also added to certain dye solutions to alter the hue or intensity of the resultant pigment, creating substrates that would contain tin and possibly aluminum, if alum was also used (Kirby et al. 2005). There were complex variations of the laking process employed by the nineteenth century, which included the addition of a variety of metal salts containing aluminum, tin, calcium, lead, iron, antimony, copper, and chromium (Riffault et al. 1874). Additionally, scarlet lakes were sometimes produced by precipitating a cochineal lake in the presence of vermilion (HgS) (Bearn 1923). Eventually, scarlet lakes were made by precipitating alizarin crimson directly on or mixing it with the pigment vermilion (Church 1915). The choice of substrate and corresponding formula was often determined by the desired color of the pigment. Aluminum-calcium substrates, for example, were typically used in certain yellow lake pigments as well as “rose-pink” Brazilwood lake pigments (Kirby and White 1996).

Preparation of Lake containing Oil Paint Films

This study focused on the characterization of two lakes with an aluminum containing substrates, one with aluminum and calcium, and one with aluminum and tin. The dyes were extracted directly from the dyestuff into an alkali solution before precipitating to ensure that any inorganic elements detected were directly associated with the dyestuff. The four analyzed lake pigments were lac lake, cochineal lake containing calcium, cochineal carmine naccarat, and madder-tin lake. The source for the calcium containing cochineal lake was available to the authors from a supply that they produced for another study. Additionally, its recipe was known and recorded, and it had the sought-after inorganic substrate. The carmine pigment was purchased rather than made in-house as the authors had did not have access to the necessary equipment and had difficulty reproducing a carmine naccarat of the quality associated with the historical pigment. All lakes were ground and dispersed into their binders using a glass muller on a roughened glass plate. Subsequent paints were then applied to a Mylar support and analyzed with the ARTAX Micro XRF unit (equipped with a helium purge) and the Bruker handheld XRF unit (equipped with a vacuum). The addition of a vacuum and helium purge enables detection of elements as light as sodium and a more accurate reading of aluminum (McGlinchey 2012). All mordants are expected to show peaks of Al, as alum ($Al_2(SO_4)_3H_2O$) was a component, to a greater or lesser extent, in all of the analyzed lakes. Additional paint films were prepared by adding each red lake pigment into lead white-containing linseed oil. The resulting films were: lac lake and lead white, carmine and lead white, madder tin and lead white, and cochineal calcium lake and lead white.

Analysis of Aluminum Substrates in Lake-Containing Oil Paints

Overall, the ARTAX proved most successful and read higher concentrations of aluminum in lac lake, tin in madder lake, and calcium in cochineal lake. Even with a vacuum, the Bruker handheld detected negligible traces of aluminum. Aluminum peaks were suppressed in all samples containing the red lakes mixed with lead white paint. Aluminum was detected in three of the four red lakes; these results were observed using both XRF units (see Table 2). As with Table 1, the approximate concentrations of aluminum listed in Table 2 are the reported values (after calibration has been carried out); this is particularly evident in the case of the handheld unit, which was unable to detect any aluminum in some of the samples. No aluminum was found in the cochineal carmine paint using either the ARTAX or the Bruker handheld XRF unit (Table 2). The helium purge and vacuum were ineffectual in the detection of aluminum in carmine. While the pigment was purchased commercially, recipes for carmine that the authors have consulted often contain a minimum of alum, far less than most lakes, and a reduced detection was expected. For example, an aluminum concentration of 8,742μg/cm2 was detected when analyzing the lac lake sample using the ARTAX unit (equipped with the helium purge), but aluminum was undetectable when the lac lake was mixed with lead white oil paint. Similar effects were noted with other lighter elements. For example, traces of sulfur that previously read as 25,520μg/cm2 in the madder sample using the ARTAX unit were undetectable in the same sample mixed with lead white oil paint. These results confirm previous observations and studies as lead is known to absorb the fluorescence generated by lighter elements (McGlinchey 2012).

Case Study: XRF Analysis of a painting attributed to Adolphe Monticelli

XRF analysis was performed on Flower Still Life (c. 1890s, University of Delaware) attributed to the French painter Adolphe Monticelli using the Bruker handheld unit. Analysis of translucent, deep scarlet-colored brushstrokes revealed the presence of iron, lead (likely from the lead-white ground due to the attenuated pattern of the La1 and Lb2 peaks), tin, and trace amounts of calcium, manganese, and mercury (Figure 2). In addition, a trace amount of copper was found to originate from the handheld unit (likely the metallic housing) as confirmed by performing a series of blank reference spectra. Additional spot analyses revealed a similar pattern of trace elements (Ca, Mn, and Hg) with varying amounts of lead, chromium, and iron; however, no tin could be detected save for areas containing deep scarlet-colored paint. While it is theoretically possible that metal salts containing aluminum, calcium, lead, iron, and chromium are present as mordants for this particular red lake, the absence of tin in all other regions of the painting points towards tin as the likely mordant (Riffault et al. 1874). For comparative purposes, the same handheld XRF unit was then used to analyze Bouquet (c. 1875) at the Philips Collection in Washington, DC, as this painting possesses a more secure attribution to Monticelli. Analysis of deep scarlet-colored brushstrokes revealed a similar pattern as seen in the XRF spectrum shown in Figure 2, again suggesting the use of a tin-mordanted lake. These results correspond to other findings relating to Monticelli's works as the artist appears to have favored tin-mordanted cochineal lake (Stoner and Morrison 2012). In addition, Stoner and Morrison were able to detect trace amounts of vermillion, red earth, and chrome yellow in what appeared to be relatively pure passages of red lake paint (possibly due to unintentional mixing as Monticelli would often apply his colors into still-wet paint). As this tin-mordanted red lake has been found in several other paintings associated with the artist, its presence should be considered when dealing with questions surrounding attribution as well as the identification of spurious works (Stoner and Morrison 2012).

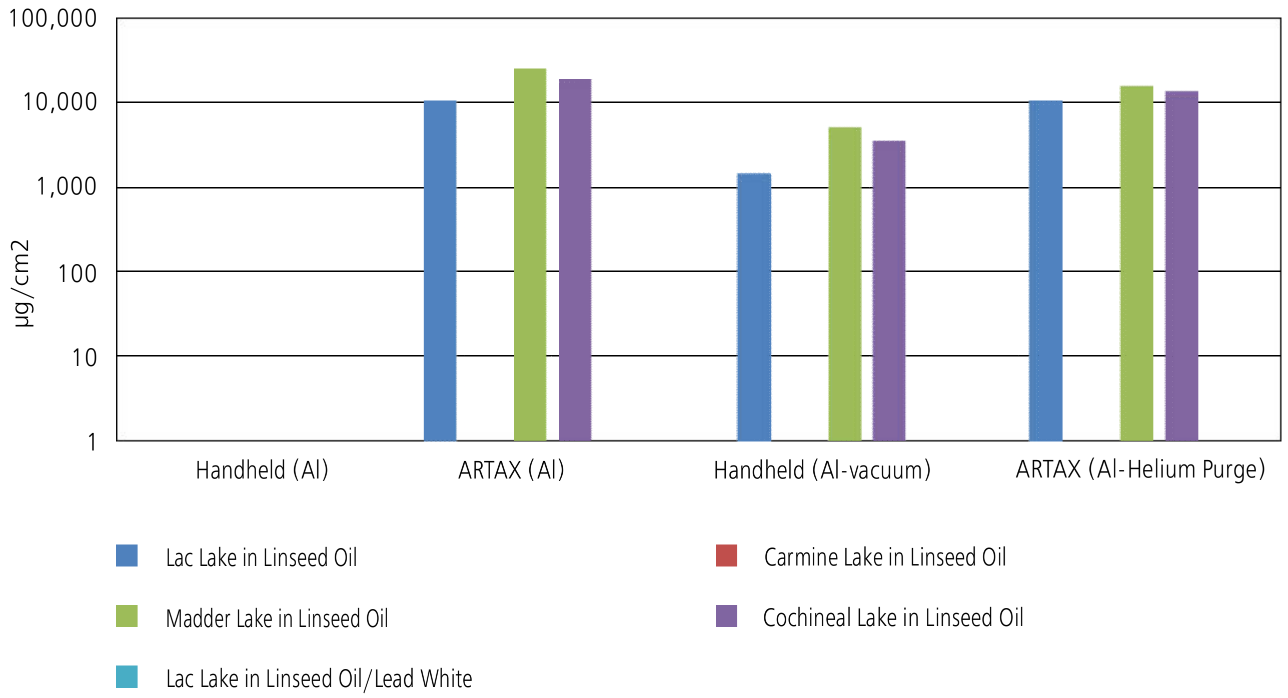

Table 2

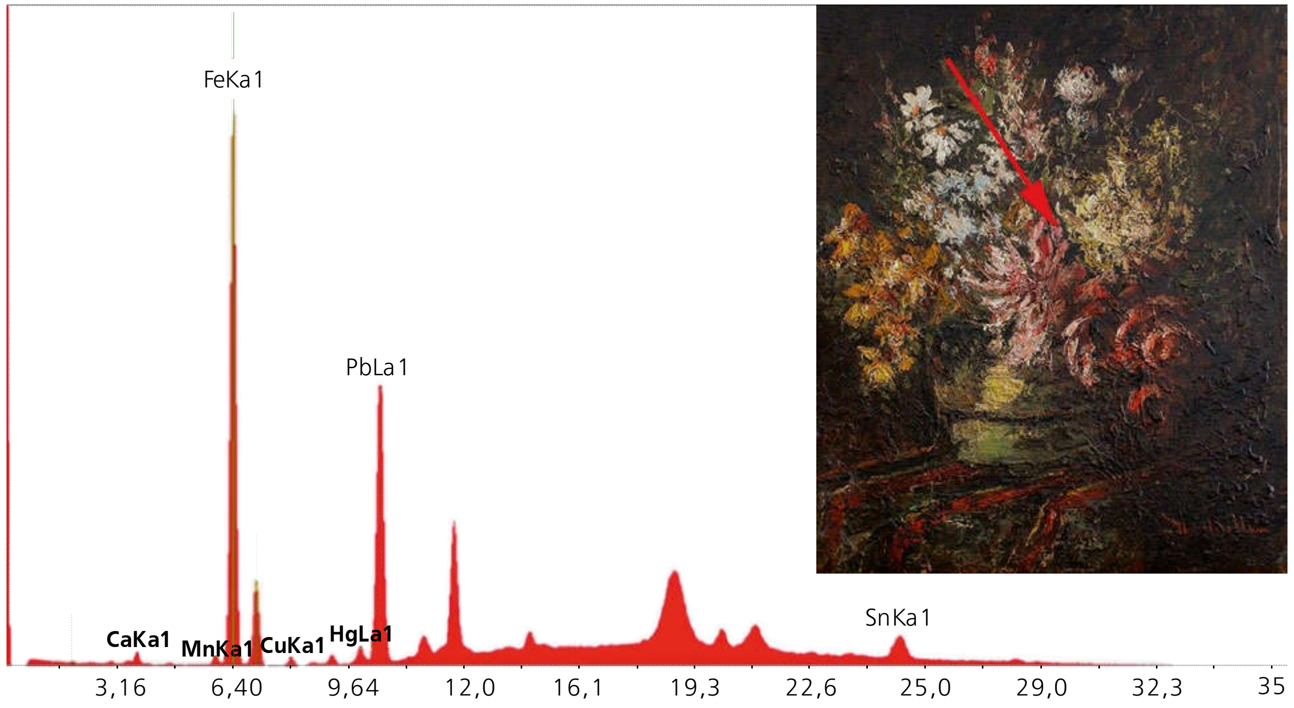

Figure 2

LAPIS LAZULI

History of Use and Types of Lapis Lazuli

Natural, refined ultramarine pigment has been highly regarded for its brilliant blue color since antiquity. Ultramarine was made by physically refining ground lapis lazuli in a process developed by the Arabs and adopted in Europe around the twelfth century (Plesters 1993). Its use diminished dramatically with the invention of synthetic ultramarine in the nineteenth century. The coloring component in lapis lazuli and natural ultramarine is lazurite, a complex, sulfur-containing sodium alumino-silicate. Aluminum, sulfur, and sodium are the signature defining elements when characterizing a natural ultramarine pigment using XRF techniques. Residual calcium from calcite and possibly pyrite impurities can also be present even in the most refined natural pigment (Plesters 1993).

Preparation of Natural Ultramarine (Lapis Lazuli) Samples

The natural ultramarine paint films were made from Dr. George Kremer's highest grade, "Fra Angelico Blue" ultramarine. Kremer states that this is made using historically accurate methods (Kremer Pigments 2016). The pigment was ground into the appropriate binder and thickly painted onto thin-film Mylar substrates both with and without the addition of lead white pigment. While sulfur, sodium, and other trace elements can be present in natural ultramarine samples, the authors focused primarily on aluminum so that they could compare these results with those obtained from their analysis of lake pigments. Aluminum can be difficult to detect due to the low excitation efficiency of XRF technology (McGlinchey 2012). This difficulty may be the reason why a recent study on the analysis and detection of nineteenth-century blue and green pigments using XRF and Raman spectroscopy was only able to successfully detect ultramarine using the latter analytical method (Rosi et al. 2004). The natural ultramarine samples were analyzed using the ARTAX unit with and without the helium purge and handheld XRF unit under vacuum. The results are summarized in Table 3.

As with Tables 1 and 2, the approximate concentrations listed in Table 2 are the reported values (after calibration has been carried out); this is particularly evident in the case of the handheld unit which was unable to detect any aluminum unless the analysis was performed using the vacuum.

Analysis of Natural Ultramarine (Lapis Lazuli)

Aluminum peaks in all natural ultramarine samples could not be detected with the handheld unit unless the system was equipped with a vacuum purge (see Table 3). However, observed aluminum concentrations were extremely low even with the vacuum (1,887µg/cm2), generating peaks that were at times indistinguishable from the background signal. In addition, the relative concentrations of sulphur were also significantly low unless the vaccum unit was used. The ARTAX unit was able to successfully detect aluminum in the ultramarine paint samples with and without a helium purge (concentrations at around 7,663µg/cm2 and 3,943µg/cm2, respectively). As observed in the analysis of red lake paint samples, the presence of lead white completely hindered the detection of aluminum using both units, even with the additional helium purge and vacuum attachments. These results suggest that certain handheld XRF units may not be able to detect the signature peaks associated with aluminum at certain concentrations and therefore may not be reliable for the characterization of lapis lazuli.

Case Study: XRF Analysis of paintings by Thomas Wijck

XRF analysis was performed on two seventeenth-century paintings by Thomas Wijck housed at the Chemical Heritage Foundation in Philadelphia: An Alchemist and The Alchemist in His Studio c. 1640–1677 (Figure 3). Art historians were interested in characterizing the pigments present in the brilliant blue passages on both paintings. These areas were analyzed using the handheld XRF unit both with and without the vacuum. No peaks associated with aluminum were detected in either painting, although significant amounts of calcium and iron were detected. In both instances, a trace amount of copper was found to originate from the handheld unit (likely the metallic housing) as confirmed by performing a series of blank reference spectra. Commonly used blue pigments during this particular period include smalt, azurite, lapis lazuli, and indigo (Prussian blue was not in use until the early 18th century). The absence of aluminum and other characteristic elements associated with these blue pigments (e.g. copper, cobalt) should not automatically suggest the use of an organic blue pigment such as indigo as mass absorption effects (often created by the presence of lead) can lead to low detection limits. Additional analytical techniques are therefore required to characterize these blue paint passages in order to avoid misinterpretation and/or mischaracterization of Wijck's preferred palette.

CONCLUSION

Many conservation labs are now using a handheld XRF instrument as their primary tool for characterizing inorganic materials. This can complicate interpretation, however, as hand-held units (even when equipped with a vacuum) still have a difficult time finding signature peaks associated with lighter elements. Even when XRF analysis is used to gather elemental data within the correct parameters, the information must be interpreted with a full understanding of the possible influence of lakes, driers, and oil mediums that can also contain similar elements. While Bruker has since manufactured additional handheld models that have improved detection capabilities (such as the Tracer 5i), many professionals working in cultural institutions continue to rely on the Tracer III-SD model and, therefore, may find the information summarized in this study applicable to their research. As recent advancements in technology have allowed for the application of macro-XRF scanning units to the study of easel paintings, the analyst must possess a greater awareness of these materials. The influence of aluminum, tin, and other inorganic components in organic lakes should also be considered when interpreting XRF data, as mixtures of different pigments may suppress the detection of elements that are actually present. Finally, this study confirms that it may be difficult or impossible to detect aluminum or other lighter elements in lakes and lapis/ultramarine pigments when they are admixed with lead containing media.

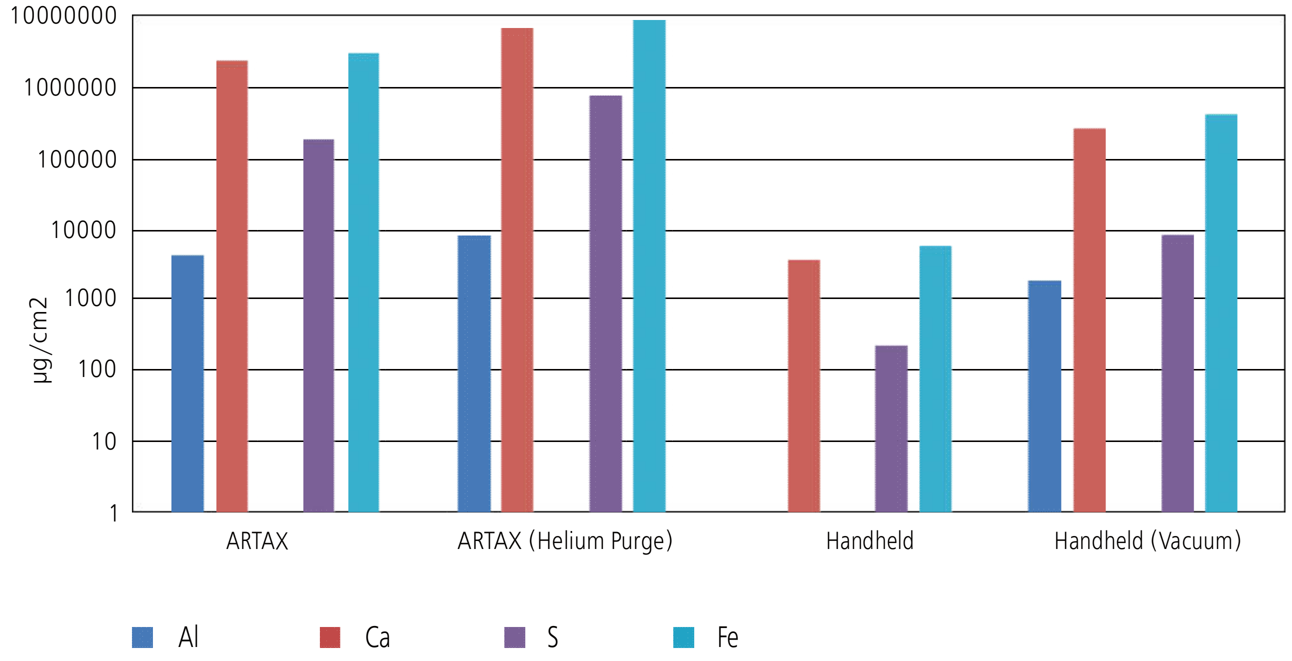

Table 3

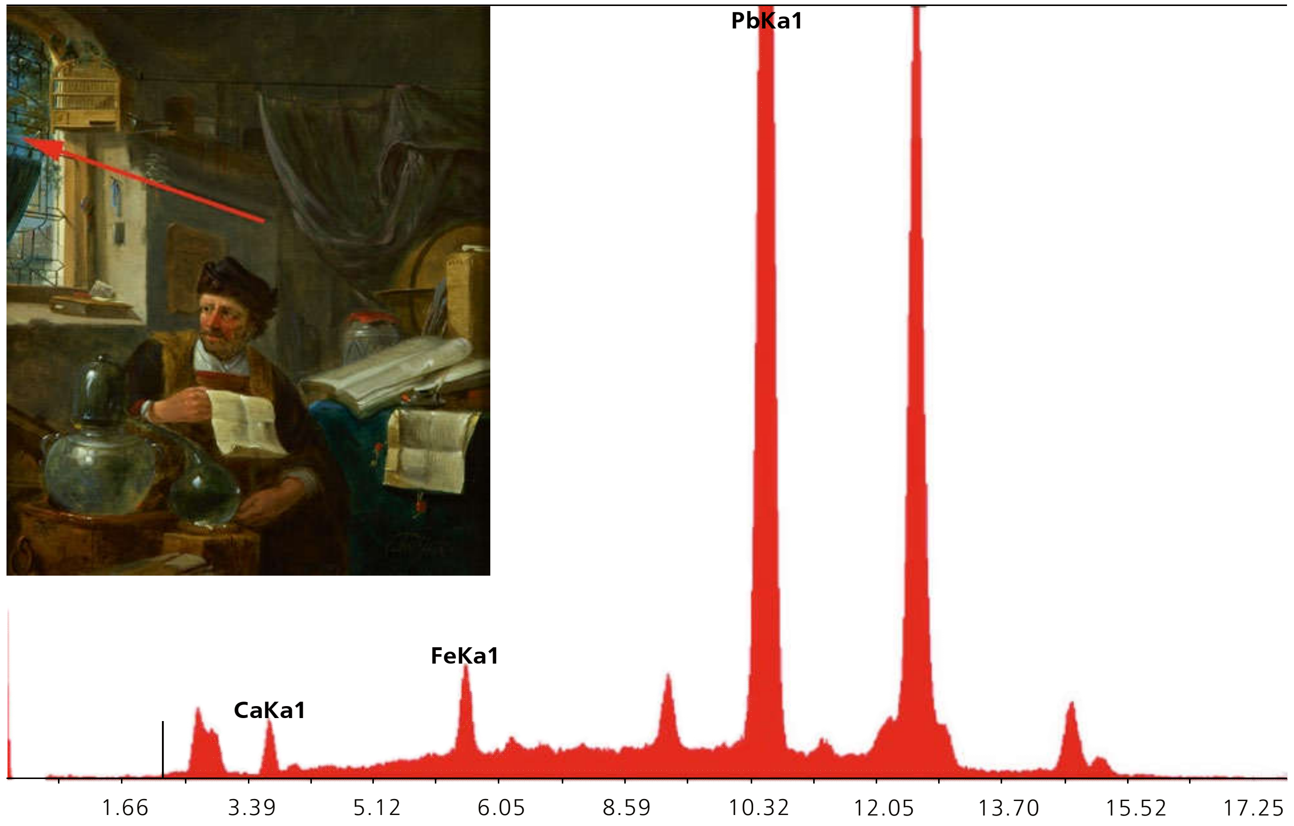

Figure 3

ACKNOWEDGEMENTS

We are indebted to the Getty Conservation Institute for the loan of their thin-film standards. This research would not have been possible without the help and input of Dr. Jennifer Mass, then head of Winterthur's Scientific Research and Analysis Laboratory (SRAL). The authors also want to thank SRAL's Catherine Matsen for her constant assistance. Kelsey Mellow was also invaluable in her work in the creation of the red lake pigments and help running the thin-film standards. Finally, we want to mention the essential support and encouragement offered by Dr. Joyce Hill Stoner and Debra Hess Norris from the Winterthur/University of Delaware program in Art Conservation.

SUPPLIERS OF EQUIPMENT AND MATERIALS

Cochineal insects, stick lac (unprocessed shellac resin), gum Arabic, madder roots, raw umber pigment, highest-grade natural Afghanistan ultramarine (refined using traditional methods), calcite (natural calcium carbonate), alum (aluminum potassium sulfate), carmine naccarat from cochineal, potassium carbonate, Swedish cold-pressed linseed oil, and mastic resin were purchased from Kremer Pigments, Inc., New York, NY, USA. Lead white (prepared using the Dutch Stack Method) and vermilion (dry process), were purchased from Rublev/Natural Pigments, Willits, CA, USA. Raw samples of Afghanistan lapis lazuli were purchased from Pakistan Onyx and Marble 4304 Cherry Blossom Dr, Ypsilanti, Michigan, USA. Litharge (lead monoxide) and zinc sulfate were taken from an unspecified source and confirmed using XRF. Lead acetate and tin (IV) chloride were purchased from Fisher Scientific, Pittsburg, PA. USA. The study used Winsor and Newton English distilled turpentine and Grumbacher Cobalt Drier was used for the cobalt napthenate. These two items were purchased at a local art supply store.

RECIPES

Lac lakes

20g of ground stick lac was added to 500 ml demineralized water in a large glass beaker. These were allowed to set overnight. 20g of potassium carbonate was then added and the whole was heated to 80°C. The whole was allowed to cool and the solution was filtered to remove residual resin and other particulates. The filtered solution was again heated to 80°C. 120g of alum (aluminum potassium sulfate) was added to a beaker containing 150 ml of demineralized water and heated to dissolve. The alum solution was allowed to cool and then added to the dye solution with continual stirring. The mixture was stirred while the pigment precipitated until the effervescence ceased. The pigment was allowed to settle, and the liquid poured off of the top. The container was filled with fresh demineralized water and the pigment was allowed to again settle. This procedure was repeated until there was no evidence of free dye and the liquid was completely clear. The water was then poured off and the pigment was dried in a drying oven at 50°C. The dried lake was then crushed and ground using a porcelain mortar and pestle.

Cochineal with aluminum and calcium substrate

20g of ground cochineal insects were added to 600 ml demineralized water in a large glass beaker. These were allowed to set overnight. 20g of alum was then added and the whole was boiled for an hour to extract the dye. The whole was allowed to cool and then filtered to remove residual insects and other particulates. The filtered solution was again heated to 80°C. 60g of natural chalk was slowly added to the hot solution while stirring to precipitate the pigment. The addition of chalk was stopped when precipitation ceased. The pigment was allowed to settle and the liquid poured off of the top. The container was filled with fresh demineralized water and the pigment was allowed to again settle. This procedure was repeated until there was no evidence of free dye and the liquid was completely clear. The water was then poured off and the pigment was dried in a drying oven at 50°C. The dried lake was then crushed and ground using a porcelain mortar and pestle.

Rose madder lake with tin

20g of ground madder root was added to 600 ml demineralized water in a large glass beaker. This was allowed to set overnight. The whole was heated to 70°C for an hour to extract the dye. 0.16g alum was then added and boiled for an additional five minutes. This was allowed to cool, and the solution was filtered to remove the remaining root and other particulates. The solution was then heated to 50°C. 20 g of tin (IV) chloride was dissolved in demineralized water. This was then immediately added dropwise into the hot dye solution with continual stirring to precipitate the pigment. After precipitation, the pigment was allowed to settle, and the clear liquid poured off of the top. The container was then filled with fresh demineralized water and the pigment was allowed to settle again. This procedure was repeated until there was no evidence of free dye and the liquid was completely clear. The water was then poured off and the pigment was dried in a drying oven at 50°C. The dried lake was then crushed and ground using a porcelain mortar and pestle.

Leaded linseed oil

17.6g of litharge (lead monoxide) was added to a stainless-steel pan containing 355 ml of cold pressed linseed oil. The two were stirred together and slowly heated with stirring to 230°C. The whole was allowed to cool to 100°C and strained to remove undissolved particles. The leaded oil was poured into a glass jar, sealed, and aged for six months. The clear leaded oil was then decanted from the precipitate.

Megilp

Heavy mastic varnish was made by dissolving 50g of fresh mastic resin in 100 ml of gum turpentine. The varnish was allowed to rest for a week and then decanted and strained to remove impurities. Megilp was made by mixing equal volumetric parts of the heavy mastic varnish with the leaded linseed oil (see above).

Gumption (Adapted from Ibbetson in Carlyle 2001 pages 394–5)

85.05g washed and dried mastic resin was ground with 28.35g lead acetate on a glass plate using a muller to make a smooth, butter-like paste.

Coarse drying oil (Scaled down and adapted from Dossie, Recipe 1 in Carlyle 2001 page 349)

212 ml of cold pressed linseed oil, 6.40g gum Arabic, 25.50g litharge, 6.40g lead acetate, 12.75g zinc sulfate, and 6.40g raw umber pigment were slowly heated and stirred together to 250°C until they were completely incorporated and the solution was complete. The whole was then cooled to 60°C and 212 ml gum turpentine was added. The whole was poured into a glass jar, sealed, and aged for six months. The clear oil was then decanted from the precipitate.

Procedure for Making Oil Paint

Oil paint was prepared by placing the appropriate amount of pigment on a sheet of tempered glass. The binder was then added dropwise until a semi-dry paste was obtained by mixing with a metal palette knife. The whole was then mulled using a ground glass muller. This was continued for a few minutes and the consistence was then checked. Additional binder or pigment was then added depending upon the consistency of the paint. The paint was then mulled again for ten minutes. The final consistence was deemed appropriate when the paste retained gloss but remained stiff enough to hold its shape when manipulated with the palette knife.

References

1. Alfeld, M., Siddons, D. P., Janssens, K., Dik, J., Woll, A., Kirkham, R. & Wetering, E.v.d. 2012. Visualizing the 17th century underpainting in Portrait of an Old Man by Rembrandt van Rijn using synchrotron-based scanning macro-XRF. *Applied Physics* A, 111: 157–64.
2. Alfeld, M., Vaz Pedrozo, J., van Eikema Hommes, M., Van der Snickt, G., Tauber, G., Blaas, J., Haschke, M., Erler, K., Dik, J. & Janssens, K. 2013. A Mobile Instrument for in situ Scanning Macro-XRF Investigation of Historical Paintings. *Journal of Analytical Atomic Spectrometry,* 28: 760–67.
3. Bearn, J. G. 1923. The chemistry of paints, pigments, and varnishes. *Journal of the Society of Chemical Industry* 42(52): 1257–1258.
4. Bellettiere, S. J., and Mahoney, D. M. 1987. Multi-metallic complexes: the next generation of driers. *Journal of Coatings Technology* 59: 101–108.
5. Bomford, D., Dunkerton, J., Gordon, D., and Roy, A. 1989. *Art in the making: Italian painting before 1400.* London: The National Gallery of Art. 182–185.
6. Bonizzoni, L., Galli A., Poldi, G., and Milazzo M. 2007. In situ non-invasive EDXRF analysis to reconstruct stratigraphy and thickness of Renaissance pictorial multilayers. *X-Ray Spectrometry*. 36(2): 55–61.
7. Boughton, E. W. 1916. Effect of certain pigments on linseed oil. *Technologic Papers of the Bureau of Standards.* 71: 12.
8. Bryk, N. E. V. 2002. How is shellac made? In *How products are made: an illustrated guide to product manufacturing,* ed. D. S. Blanchfield. Detroit: Gale Group.
9. Carlyle, L. 2001. *The artist's assistant: oil painting instruction manuals and handbooks in Britain 1800–1900 with reference to selected eighteenth-century sources.* Archetype Publications. 35–37, 48–22, 101–109, 349–352, 395–402.
10. Church, A. H. 1915. *The chemistry of paints and paintings.* 4th ed. London: Steeley Service Company Limited. 208.
11. De Viguerie L., Walter, P., Laval, E., Mottin, B., and Solé V. A. 2010. Revealing the sfumato technique of Leonardo da Vinci by X-Ray fluorescence spectroscopy. *Angewandte Chemie* 122(35): 6261–6264.
12. Dik, J., Janssens, K., van der Snickt, G., van der Loeff, L., Rickers, K. & Cotte, M. 2008. Visualization of a Lost Painting by Vincent van Gogh Using Synchrotron Radiation Based X-ray Fluorescence Elemental Mapping. *Analytical Chemistry*, 80: 6436–6442.
13. Eastlake, C. L. 1960; 2001. *Methods and materials of painting of the great schools and masters.* Mineola, New York: Dover Publications. 28.
14. Elm, A. C. 1934. A century of progress in driers. ACS *Journal of Industrial Engineering Chemistry* 26(4). 386–388.
15. Gettens, R. J., Kühn H., and Chase, T. W. 1993. Lead white. *Artists Pigments: a Handbook of their History and Characteristics 2.*
16. Harley, R. D. 1982; 2010. *Artists' pigments c.1600–1835.* 2nd ed. London: Butterworth-Heinemann. 134.
17. Helwig, K. 2007. Iron oxide pigments: Natural and synthetic artists pigments. Artists Pigment *Handbook of Their History and Characteristics 4.* Washington, DC: The National Gallery of Art. 51: 66–67.
18. Hofenk de Graaff, J. H. 2005. *The colorful past: origins, chemistry, and identification of natural dyestuffs.* London: Archetype Publication. 85.
19. Kirby, J., Spring M., and Higgitt, C. 2005. The technology of red lake pigments manufacture: study of the dyestuff substrates. *National Gallery Technical Bulletin* 26: 71–87.
20. Kirby, J., White, R., 1996. The technology of red lake pigment manufacture: study of the dyestuff substrates. *National Gallery Technical Bulletin* 17: 56–80.
21. Kirby, J. Von Bommel, M., and Verhecken, A. 2014. *Natural colorants for dyeing and lake pigments.* London: Archetype Publications.
22. Kremer Pigments 2016 On-line catalog. http://shop.kremerpigments.com/en/pigments/kremer-made-and-historic-pigments/lapis-lazuli--pure-10530:.html
23. Lutzenberger, K., Stege, H., and Tilenschi, M. 2010. A note on glass and silica in oil paintings from the 15th to the 17th century. *Journal of Cultural Heritage.* 11(4): 365–372.
24. Maroger, J., and Beckham, E. 1948. *The secret formulas and techniques of the masters.* New York: The Studio Publications.
25. Mayer, L., and Myer, J. 2002. Old master recipes in the 1920s, 1930s, and 1940s: Curry, Marsh, Doerner, and Marioger, *Journal for the American Institute of Conservation* 41(1). 21–42.
26. Mayer, R. 1957. *The artist's handbook of materials and techniques.* New York: The Viking Press. 217.
27. McGlinchey, G. 2012. Handheld XRF for the examination of paintings: proper use and limitations. In *Studies in Archeological Science: Handheld XRF for Art and Archeology, ed. Shugar, A. N., and Mass, J. L.* Leuven: Leuven University Press. 131, 135, 150–151.
28. Phenix, A., and Townsend, J. 2012. A brief survey of historical varnishes in conservation. In *Conservation of easel paintings.* London: Routlidge. 254–255.
29. Plesters, J. 1993. Ultramarine blue, natural, and artificial. *Artists Pigments: A Handbook of Their History and Characteristics* 2. 36–39, 42.
30. Ritcher, J. P., 1883. The Literary Works of Leonardo da Vinci, vol. 1. London: Sampson Low, Marston, Searle & Rivington, 319–322.
31. Riffault, M. M., Toussaint, A., and Vergnaud, A. D. 1874. *Colors for painting: a practical treatise on the manufacture of colors for painting.* Philadelphia, Pennsylvania: Henry Carey Baird. 458–495, 583–585.
32. Rosi, F., Miliani, C., Borgia, I., Brunetti, B., and Sgamellott, A. 2004. Identification of nineteenth century blue and green pigments by in-situ x-ray fluorescence and micro-raman spectroscopy. *Journal of Raman Spectroscopy* 35: 610–615.
33. Schweppe, H., and Winter, J. 1997. Madder and alizarin. *Artist's Pigments: A Handbook of Their History and Characteristics* 3. 119–121.
34. Smith, C. S., and Hawthorne, J. G. 1974. Mappae clavicula: a little key to the world of medieval techniques. *Transactions of the American Philosophical Society* 64: 1–128.
35. Stoner, K., and Morrison R. 2012. Adolphe Monticelli: the materials and techniques of an unfashionable artist. *National Gallery Technical Bulletin* 33. 50–72.
36. Steele, L. L. 1924. Effects of certain metallic soaps on the drying of raw linseed oil. *Industrial and Engineering Chemistry* 16: 957.
37. Tumosa, C. S., and Mecklenburg, M. F. 2005. The influence of lead ions on the drying of oils. *Reviews in Conservation* 8: 41–42.
38. White, R., and Kirby, J. 1994. Rembrandt and his circle: seventeenth-century Dutch paint media reexamined. *National Gallery Technical Bulletin* 15: 69, 71.