APPLICATIONS OF X-RAY DIFFRACTION IN CONSERVATION SCIENCE AND ARCHAEOMETRY

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ABSTRACT

This paper presents case studies that illustrate the usefulness of X-ray diffraction in the field of conservation science and archaeometry. X-ray diffraction was instrumental in discovering new pigments such as a yellow lead silicate sulfate chloride of the ellestadite group found on fresco fragments from an Abbasid structure built in the early eight century A.D. in Jordan; the yellow compound pararealgar (As₄S₄), which was identified for the first time in a painting; and magnesium cobalt arsenate, a violet pigment found in numerous paintings. X-ray diffraction also helped answer questions related to degradation processes: crystals forming on artifacts in a Canadian museum were identified as cyclohexylamine hydrochloride (C₆H₁₃N·HCl). This finding was key in tracing the source of the problem back to vapour phase corrosion inhibitors used in the museum’s steam humidification system. Badly corroded metal fillets on a Boulle clock proved to be made of tin amalgam, which is susceptible to galvanic corrosion, instead of the more stable pewter. X-ray diffraction analysis of multi-layer samples is also discussed in relation with the later case study and with the study of paint samples taken from polychrome elements of the sculpted décor of the Ursulines chapel, Québec City.

INTRODUCTION

The analysis of works of art and museum objects is usually done to answer two types of questions. First, there are questions related to the stability or deterioration of materials used to make the objects. These questions must be answered to ensure the proper conservation of the objects, whether through preventive conservation or treatment. Second, there are questions related to the date of execution or manufacture, country of origin, or material history of the objects; such studies fall within the field of archaeometry. Although several physical and chemical methods can, and often must, be used to answer both types of questions, X-ray diffraction plays an important role in the study of works of art and museum objects.

Taking relatively large samples of degradation or corrosion products from artistic and historical objects is often acceptable, since such products will generally be removed anyway as part of a conservation treatment. However, the removal of samples of original material from unique and irreplaceable works of art and museum objects is limited to microscopic amounts. This article will present examples that will illustrate the challenges posed by the analysis of such small samples and the usefulness of microdiffractometry and diffractometry in conservation science and archaeometry.
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INSTRUMENTATION

Although the goal of this article is not to review the instrumentation available for XRD analysis of microsamples, it is relevant to describe the system currently used at the Canadian Conservation Institute (CCI) to better understand the challenges posed by the subsequent case studies and to appreciate the contribution of X-ray diffraction to problem solving.

At CCI, analysis of very small volumes of powder used to be performed using a fixed-tube generator and a Gandolfi camera. Samples had to be measured for several hours, typically overnight. In the late 1980s, a major turning point in X-ray diffraction was the introduction of the microdiffractometer, which soon began to be used in conservation science [1–3]. The system currently used at CCI (which was acquired in 1990) is a Rigaku rotating anode generator equipped with a conventional θ-2θ goniometer, a mount for a Gandolfi camera, and a microdiffractometer. The microdiffractometer includes a goniometer with a triple-axis sample oscillation mechanism (ω, χ, φ), an X, Y, Z stage, and a goniometer head. A built-in 160x microscope allows positioning of the sample in the path of the X-ray beam. Collimators of various apertures (10, 30, 50, and 100 μm) are placed in a collimator holder to adjust the size of the X-ray beam. The X-ray detection is handled by a curved, position-sensitive, proportional counter (PSPC) and a multi-channel analyser. One of the advantages of the microdiffractometer is the great reduction in measurement time for very small samples, especially when used in conjunction with a rotating anode X-ray generator.

Analysis of samples from works of art and artifacts is now being done exclusively with the microdiffractometer. Analysis of samples that can be obtained in larger quantities can sometimes be done by diffractometry using a low background sample holder, while analysis of very large samples such as standards and reference materials is done by diffractometry and does not usually require any special type of sample holder. Most of the following case studies have been previously discussed and details about experimental conditions for each sample can be found in the references provided.

CASE STUDIES

Discovery of a new yellow pigment [4]

Frescoes from an Abbasid qasr (the Arabic word for manor estate) built in the early eighth century A.D. were discovered in al-Humeima, Jordan. The colours white, beige, yellow, brown, grey, black, two shades of red, and two shades of orange were observed on the frescoes. Analysis of paint samples showed that the black and brown paints were mixtures of dark red and dark orange iron earth pigments with a black pigment, which was tentatively identified as charcoal black. The shades of red were obtained by using red ochre and calcite in various proportions. The orange pigment was identified as an orange iron earth pigment, similar to modern examples of burnt sienna. However, the yellow pigment from the qasr was found to be a compound which had not previously been reported as being used as a pigment.
The paint layer, although having a greenish tint at the surface, has a bright yellow colour when observed in cross-section. It was found by SEM/EDS to contain primarily lead (Figure 1). The paint layer, although very thin (approximately 2 μm), can easily be distinguished from the support in the SEM image because of the large difference in atomic number between lead and calcium. In addition to lead, minor amounts of calcium, chlorine, magnesium, silicon, and phosphorus, and traces of aluminum, potassium, and iron were also detected in the paint layer.

![SEM photomicrograph (left) and X-ray map (right) of a cross-section prepared from the yellow fresco fragment.](image)

The X-ray pattern of the yellow paint closely matched data published on two very similar lead silicate sulfate chloride compounds from the apatite group (general formula $A_{10}(XO_4)Z_2$). The first compound is the yellow, synthetic lead-ellestadite, $\text{Pb}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3\text{Cl}_2$ (PDF 41-475) [5]. The second compound, the mineral mattheddleite, $\text{Pb}_{20}(\text{SiO}_4)_7(\text{SO}_4)_4\text{Cl}_4$, is described as being colourless (PDF 41-610) [6]. No attempts were made to perform quantitative analysis to determine the exact chemical formula of the yellow compound, as it was known, based on the SEM/EDS analysis, to be mixed with other minerals.

Such a pigment has never been identified on frescoes from other sites, suggesting that the mineral was found locally. The lemon-coloured lead-ellestadite would have been an alternative to the golden yellow ochre, the only yellow pigment which was considered suitable for frescoes [7].

*The occurrence of pararealgar as a pigment [8]*

A painting entitled *Holy Family and Saint* (Winnipeg Art Gallery, accession number G36-107) was examined to determine if its materials or structure would provide evidence for a date or period of execution. The following pigments were identified in the painting: azurite, lead tin yellow type I, lead white, verdigris or copper resinate, and pararealgar. The ground was found to
be primarily lead white, with a small amount of neutral lead carbonate impurity present. The presence of azurite, lead tin yellow type I, and the lead white ground place the painting in the period 1500 to 1700 [9–13].

The occurrence of pararealgar in paintings had never been reported. Pararealgar, an arsenic(II) sulfide polymorph, was reported and named pararealgar by Roberts et al. in 1980 [14]. This yellow mineral was found in two geological locations in British Columbia, Canada, where it partially or completely replaced realgar in stibnite-bearing quartz veins. The mineral has also been found at other localities in North America and Europe. The new mineral and the name pararealgar were approved by the Commission on New Minerals and Mineral Names. Pararealgar was characterized by several techniques, including X-ray diffraction.

The only arsenic sulphide compounds that had been known as pigments were the minerals realgar and orpiment. Both minerals have been used as pigments since antiquity and have been discussed extensively in the conservation literature [15]. Realgar is the red-orange arsenic(II) sulfide (As$_4$S$_4$) and orpiment is the yellow arsenic(III) sulfide (As$_2$S$_3$). In the past, pararealgar may have been misidentified as orpiment if it was characterized solely on the basis of colour and elemental analysis. Before 1980, the mineral pararealgar had not been named and its X-ray diffraction data had not been reported, therefore it is possible that X-ray diffraction patterns were obtained which did not match that of orpiment, without any mention of the discrepancy being made in the literature. In fact, several museum laboratories revisited their X-ray diffraction data after the occurrence of pararealgar was published in 1995 [8] and since then the number of occurrences found has increased. It is likely that information about when and where pararealgar was used as a pigment will emerge when a larger number of occurrences has been reported.

**Characterization of cobalt violet [16]**

Cobalt violet is reported in most books on artists’ pigments as corresponding to either cobalt phosphate or cobalt arsenate [17–19]. Several sources mention that the colour of cobalt phosphate varies with its hydration state. Three compounds are commonly reported: the violet anhydrous cobalt phosphate, the violet-pink or deep violet tetrahydrate, and the pink octahydrate [20, 21]. However, very little information is found in the literature regarding the chemical formula of the light violet cobalt arsenate. Historical sources provide conflicting (and often unreliable) information, while most modern sources simply do not report a chemical formula. The third edition of the *Colour Index* states that the chemical formula of light cobalt violet corresponds to that of the mineral erythrite, *i.e.*, cobalt arsenate octahydrate [20].

While examining a painting of unknown attribution in 1996, a violet paint sample which contained cobalt and arsenic was found. The presence of cobalt and arsenic indicated that the pigment was light cobalt violet. However, the X-ray powder diffraction pattern obtained for this sample did not correspond to the experimental patterns of anhydrous or hydrated cobalt arsenate compounds reported in the PDF database. Later, the same X-ray pattern was obtained for several purple samples from paintings by Quebec artist Jean Dallaire dating from 1952 to 1962, and from samples from a palette used by the Canadian artist Frederick H. Varley towards the end of his career, in the late 1960s.
In an attempt to establish the exact chemical formula of the cobalt arsenate pigment, several commercial paints and dry pigments were analysed in order to find a pure sample of this pigment which could serve as a standard. A cobalt violet pigment from the company Roberson was found to be a pure compound of cobalt and arsenic with an X-ray pattern identical to those of the samples taken from works of art.

X-ray patterns have been reported for three cobalt arsenate compounds: the anhydrous cobalt arsenate, Co\(_3\)(AsO\(_4\))\(_2\) (PDF 10-346), the monohydrate, Co\(_3\)(AsO\(_4\))\(_2\)-H\(_2\)O (PDF 32-291), and the octahydrate, Co\(_3\)(AsO\(_4\))\(_2\)-8H\(_2\)O (PDF 33-413). The anhydrous cobalt arsenate has an orthorhombic structure. The crystal structures of three other polymorphs of cobalt arsenate have been published. One polymorph has a tetragonal structure; the other two have monoclinic structures. The calculated patterns of these three polymorphs were included in the calculated patterns that were added to the 1998 release of the PDF database. This allowed for a direct comparison of the experimental pattern of the Roberson Cobalt Violet with calculated patterns. It was found to resemble closely, but not to match exactly, the pattern of the tetragonal cobalt arsenate.

The Roberson Cobalt Violet pattern also resembled that of magnesium arsenate, Mg\(_3\)(AsO\(_4\))\(_2\) (Figure 2). Cobalt arsenate and magnesium arsenate are isostructural. They both belong to space group I-42d. The peaks in the experimental pattern of the Roberson Cobalt Violet were indexed using the same space group. The cell parameters, as well as the I/I\(_c\) ratio, were found to be in
between those reported for cobalt arsenate and magnesium arsenate (Table 1), suggesting that the Roberson Cobalt Violet could be a compound in which part of the cobalt is substituted for magnesium. Since magnesium cannot be readily detected by EDS in the presence of arsenic, its Kα line (1.254 keV) being too close to the arsenic Lα line (1.282 keV) to be resolved, the pigment was analysed by inductively-coupled plasma spectroscopy. It was found to contain 12.2 ± 0.1% (w/w) magnesium and 22.3 ± 0.1% (w/w) cobalt. The empirical formula Mg₂Co(AsO₄)₂ was calculated from these results.

Table 1. Cells parameters and I/Iₓ ratios of cobalt arsenate, magnesium arsenate and Roberson Cobalt Violet

<table>
<thead>
<tr>
<th></th>
<th>Mg₂(AsO₄)</th>
<th>Roberson Cobalt Violet</th>
<th>Co₃(AsO₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell parameters</td>
<td></td>
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<td>a (nm)</td>
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<td>0.68138</td>
<td>0.6858</td>
</tr>
<tr>
<td>c</td>
<td>1.8963</td>
<td>1.8934</td>
<td>1.8872</td>
</tr>
<tr>
<td>I/Iₓ</td>
<td>2.9</td>
<td>3.2</td>
<td>4.62</td>
</tr>
</tbody>
</table>

Since this work was published, magnesium cobalt arsenate has been identified at CCI by X-ray diffraction in other paint samples from works of art; in addition, a recently acquired scanning electron microscope equipped with a wavelength dispersive spectrometer providing higher resolution now allows the detection of magnesium in the presence of arsenic. On the other hand, cobalt arsenate, a pigment frequently mentioned in the literature on artists’ materials, has still not yet been unambiguously identified; in the case of most occurrences previously reported, cobalt arsenate was identified on the basis of the detection of cobalt and arsenic by SEM/EDS, but cobalt arsenate and magnesium cobalt arsenate cannot be distinguished by this technique.

_Crystals forming on artifacts_

Conservators at the Glenbow Museum in Calgary, Alberta, noticed that crystals were forming on some of their artifacts in both display and storage locations. They would brush the crystals off the artifacts, but the crystals would soon reappear. Crystals with similar morphology formed on objects as diverse as the leather case of a tape recorder, a sandstone sculpture, a contemporary painting, a wooden barrel, a wooden crate, and a stoneware jug.

To determine the nature and source of the crystals, small samples were removed from the artifacts and sent to CCI for analysis. Analysis by microdiffractometry showed that the crystals on all objects were crystals of cyclohexylamine hydrochloride, C₆H₁₃N·HCl.

Cyclohexylamine and other compounds such as morpholine and diethyaminoethanol, are commonly used as vapour phase corrosion inhibitors (VPIs) in steam generation and distribution systems required for industrial heating or humidification [22, 23]. VPIs are used to protect the
ferrous components of such systems from corrosion. After receiving the CCI report, the conservators found out that all three compounds were used in the museum’s steam humidification system.

Cyclohexylamine is a strong base and therefore will react with acids. The artifacts on which cyclohexylamine will crystallize as the hydrochloride salt have to be acidic; the source of chlorides, required for the salt to form, may be the artifacts themselves or external pollutants. Cyclohexylamine is a stronger base than morpholine ($K_b$ of $4.5 \times 10^{-4}$ compared to $2.1 \times 10^{-6}$ for morpholine, no data for diethylaminoethanol [24]), which means that cyclohexylamine will react first with any acid. This explains why only the cyclohexylamine salt is formed.

*Ursuline Chapel, Québec City* [25]

The most powerful application of microdiffractometry at CCI is the analysis of multi-layer samples, such as cross-sections prepared from paint samples. It is generally difficult to get a powder sample of each layer without contamination from neighbouring layers. Microdiffractometry makes analysis of each layer easy and fast, provided it is thick enough. By focussing the beam, each layer of interest is analysed individually, thus preserving sample integrity. It is therefore possible to use the same cross-sections, and to analyze precisely the same areas within the cross-sections, using different methods, such as light and fluorescence microscopy and SEM/EDS.

The sample is embedded in a polyester casting resin and sections are prepared by grinding and polishing. The resin block is ground down to a size of about 6 mm$^2$ or smaller, and mounted with double-sided tape on a cylindrical sample holder, which is held on the sample stage. The area of the sample to be analysed is located under the microscope. The X, Y, Z stage is placed in a position where the sample stage is almost perpendicular to the collimator and is kept in that position for the duration of the analysis. The sample is oscillated about the $\chi$ and $\phi$ axes. The sample holder blocks the low angle portion of the detector, therefore reflections below 20°, 2θ, are not detected.

In the following example, cross-sections of samples taken from an early 18th century sculpted *décors* were analysed. The *décors*, which includes two retables and a pulpit, was sculpted and assembled between 1726 and 1736 by Pierre-Noël Levasseur for the chapel of the Ursulines convent, in Québec City, Canada. In 1901 the *décors* was carefully dismantled and was put back in place the following year in a new chapel, built on the same location. The *décors* was adapted to the dimensions of the new chapel, which is considerably larger. The goal of the project was to study the original materials, and to examine the successive changes made to the various elements of the *décors*.

Typically, the samples contained 5 to 12 layers, with thicknesses ranging from less than 10 μm to up to 300 μm. Samples from the 1902 additions had fewer layers than those taken from the original components of the *décors*. Figure 3 shows a cross-section of a sample containing 5 layers, taken from an area of the pulpit which was likely modified or repaired in 1902, and the diffraction patterns obtained for the first, fourth and fifth layers. Patterns were obtained using the
Figure 3. Cross-section of a sample from the pulpit (magnification: 80x) (left) and X-ray patterns of layers 5, 4, and 1 (from top to bottom) (right). Phases identified: a) calcite; b) dolomite; c) lead white; d) lead carbonate; e) zinc sulfide; f) barium sulfate. Overlapping peaks have been attributed to the phase contributing the most to the intensity, except in cases of equal contributions.

50 μm collimator. The thickness of the top layer was about 90 μm; other layers ranged from 100 to 300 μm. The first layer, directly applied to the wood, corresponds to the ground layer and contains calcite (CaCO$_3$; PDF 5-586) and dolomite (CaMg(CO$_3$)$_2$; PDF 36-426); the fourth contains lead white (Pb$_3$(CO$_3$)$_2$(OH)$_2$; PDF 13-131) and lead carbonate (PbCO$_3$; PDF 5-417); the fifth layer is composed primarily of lithopone (a mixture of zinc sulphide, ZnS, PDF 36-1450, and barium sulphate, BaSO$_4$, PDF 24-1035) and also contains some calcite.

An interesting feature illustrated by this sample is the change in materials observed at some point in the succession of layers: the first paint layer applied to the ground layer (layer 2 in Figure 3) is composed of lead white; the object has been repainted twice, again using lead white (as found in layers 3 and 4), but the last overpaint layer, layer 5, contains lithopone instead of lead white. This may reflect the change in paint formulation which occurred due to growing health-related concerns about the use of lead-based paint; other white pigments such as zinc white, lithopone and titanium white gradually replaced lead white, especially in indoor and outdoor house paints.

Characterization of metal fillets [26]

The treatment of a Boulle clock from the Musée des beaux-arts de Rennes collection (accession number 871.6.1), probably dating from the seventeenth century, involved the removal of badly corroded metal fillets. The fillets were thought to be made of pewter which was often used in Boulle marquetry as were brass and copper [27]. Other ornamental motifs on the clock, also made of a grey, pewter-like metal, were in a much better state of conservation.
A sample from a corroded fillet was prepared as a cross-section (Figure 4) and analysed to determine the composition of the metal and to understand why the fillets were so badly corroded compared to other grey metal motifs. X-ray diffraction patterns of the fillet's metallic core and surrounding corrosion in the cross-section were obtained using the 50 μm collimator.

The X-ray diffraction pattern of the metal fillet matched the ICDD patterns PDF 44-1184 and PDF 48-1546 reported for mercury-tin compounds having the formula HgSn₇ and HgSn₉, respectively (Figure 5). It was also found to be similar to the pattern of an amalgam of formula HgSn₁₅ [28]. As mercury and tin have the same atomic radius of 151 pm [29], one atom can substitute for the other in an amalgam without affecting the d-spacings of the X-ray diffraction pattern. However, a change in the mercury/tin ratio would affect the intensity of the diffraction lines because of the difference in electronic density between these two elements. This is indeed the case when the intensities of the mercury-tin compounds are compared to each other (Table 2). In the case of the pattern of the metal fillet, the most intense line is at 0.29869 nm while it is at 0.203 nm and 0.204 nm for HgSn₇ and HgSn₁₅, respectively, and at 0.27825 nm for HgSn₉.

Figure 4. Cross-section of a fillet, showing the metallic core and surrounding corrosion crust (magnification: 50x).

Figure 5. X-ray pattern of the metal fillet and stick patterns of the mercury tin compounds reported in the PDF database.
However, as only a sectional plane of the fillet was measured by microdiffactometry, it is possible that the sample suffered from preferred orientation, which would affect the relative intensities of the X-ray lines. A quantitative analysis of the metal fillet for mercury and tin by SEM/EDS showed the mercury percentage to be $20 \pm 1$ wt\%, consistent with a tin amalgam of formula $\text{HgSn}_7$, and confirmed this hypothesis.

Table 2. X-ray diffraction patterns of tin amalgams*

<table>
<thead>
<tr>
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<th>HgSn$_7$ PDF 44-1184</th>
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</table>

*Lines with intensities below 10 in the reference spectra were omitted for the purpose of simplification.

The corrosion around the mercury-tin metal core was a mixture of tin (II) oxide ($\text{SnO}$, PDF 6-395) and tin (IV) oxide ($\text{SnO}_2$, PDF 41-1445). Tin amalgams are susceptible to galvanic corrosion. Contact with wood, as in the case of these fillets inserted in the wooden panels of the clock, may increase their corrosion rate.

**CONCLUSION**

X-ray diffraction is an important technique that provides compositional and structural information about unknowns. It is well suited to the analysis of small samples such as those taken from works of art and museum objects, whether they are homogeneous or multi-layer samples prepared as cross-sections. X-ray diffraction has proven particularly valuable in the analysis of pigments and has helped characterize pigments that were closely related chemically.
While the emphasis is increasingly placed on non-destructive methods, that is, methods which do not require taking samples, for the scientific examination of works of art and museum objects, X-ray diffraction provides information that is not easily obtainable otherwise. Advances in instrumentation have made it possible to considerably reduce the sample size and there is no doubt that the increased access to synchrotron facilities, which is foreseeable in the future, will make it possible to study even smaller samples. It is also possible that XRD analysis performed directly on objects, which is presently severely restricted by equipment geometry and dependent on objects size and shape, may become more practicable.

REFERENCES

[20] The Society of Dyers and Colourists and the American Association of Textile Chemists and


