

High-Resolution Non-Invasive X-ray Diffraction Analysis of Artists' Paints

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Abstract

Energy-dispersive X-ray diffraction (EDXRD) is extremely insensitive to sample morphology when implemented in a back-reflection geometry. The capabilities of this non-invasive technique for cultural heritage applications have been explored at high resolution at the Diamond Light Source synchrotron. The results of the XRD analysis of the pigments in 40 paints, commonly used by 20th century artists, are reported here. It was found that synthetic organic pigments yielded weak diffraction patterns at best, and it was not possible to unambiguously identify any of these pigments. In contrast, the majority of the paints containing inorganic pigments yielded good diffraction patterns amenable to crystallographic analysis. The high resolution of the technique enables the extraction of a range of detailed information: phase identification (including solid solutions), highly accurate unit cell parameters, phase quantification, crystallite size and strain parameters and preferred orientation parameters. The implications of these results for application to real paintings are discussed, along with the possibility to transfer the technique away from the synchrotron and into the laboratory and museum through the use of state-of-the-art microcalorimeter detectors. The results presented demonstrate the exciting potential of the technique for art history and authentication studies, based on the non-invasive acquisition of very high quality crystallographic data.

Keywords: energy-dispersive X-ray diffraction, back-reflection, non-invasive analysis, artists' paints, pigment characterisation

Research Aim

The back-reflection EDXRD technique offers a method of retrieving highly accurate crystallographic parameters irrespective of the sample morphology. The method is suited to the non-invasive study of archaeological artefacts and artworks, especially paintings. We have conducted a survey study of forty oil-based artists' paints on a test panel, as a forerunner to the investigation of paintings, to explore and understand the advantages and limitations of this technique in the context of the art history and authentication of paintings.

1. Introduction

Scientific analysis of artworks can aid in their authentication [1] and attribution [2], inform conservation and restoration strategies [3] and yield insights into historical manufacturing practices [4] and painters' techniques [5]. In particular, analysis of the chemical composition of paints and pigments has proven a rich source of information. Pigments are an incredibly diverse family of materials ranging from organic dyes to minerals to synthetic inorganic salts [6]. A wide range of analytical techniques have been utilised in the scientific analysis of paintings, including hyperspectral imaging, X-ray fluorescence (XRF) spectroscopy, Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy [7, 8]. These techniques can be employed non-invasively and each has its own advantages and disadvantages. For example, XRF methods yield elemental information that in some instances allows the presence of specific pigments to be inferred but does not yield any further insights on structural characteristics. Raman methods are widely used and can identify specific pigments, notably synthetic organic pigments [9], but is ineffective for some inorganic pigments and does not generally allow further analysis such as quantification [10]. In contrast, X-ray diffraction (XRD) is a powerful technique in materials science, allowing highly specific identification and providing additional structural information on crystalline materials, such as crystallite morphology, size/strain parameters and phase weight ratios. XRD is ideally carried out on prepared, finely powdered samples in order to ensure that relative peak intensities are reproducible which aids phase identification and permits quantitative analysis. This constraint poses a challenge in the analysis of cultural heritage objects where there is a strong reluctance to alter the object by removing samples. If curators allow the extraction of samples from the artwork at all, it is usually limited to minute samples; such micro-sampling usually leaves no changes visible to the naked eye. However, sampling from a limited number of locations may not yield representative information about the entire artefact [4] and, in any case, completely non-invasive methods are the gold standard in the scientific examination of cultural heritage artefacts.

A variety of synchrotron-based XRD methods are applied to the non-invasive study of heritage artefacts [7, 11, 12] and, in addition, several groups have developed laboratory or portable XRD instrumentation for non-invasive analysis [13-20]. Conventional laboratory instruments are not in general designed to accommodate the variety of artefact shapes and sizes encountered, though on occasions the artefacts have convenient form factors [21]. Portable instruments have in common relatively low to moderate resolution of diffraction peaks when compared to commercial laboratory diffractometers. The most common design [19, 22] applies angle-dispersive XRD with a shallow incidence angle of the X-ray beam on the artefact. The instrument must be positioned at a precise distance from the surface being studied, typically achieved using laser pointing devices. Uneven surfaces, such as impasto on paintings, can present challenges to this type of instrument and adversely affects resolution and precision. The modest resolution achievable commonly limits portable XRD to phase identification [13,14,18,19] though in some instances depth information can be retrieved [15,16] as well as texture and crystallinity [16].

Energy-dispersive XRD (EDXRD) in a back-reflection geometry has previously been shown to have very low dependence on the morphology of the sample [23-25], a characteristic that is highly desirable in the context of archaeometry. Furthermore, very high resolution can be achieved, while retaining insensitivity to sample morphology, by implementing the technique at a synchrotron facility [25]. The need to transport paintings and other irreplaceable heritage objects to a synchrotron is a disadvantage and in many cases is not allowed by galleries and museums or involves high insurance costs. However, we plan ultimately to transfer the back-reflection EDXRD technique to the laboratory and museum through the use of microcalorimeter technology. The motivation for the synchrotron-based study presented here is to explore the advantages and limitations of the technique applied to paintings, initially using representative paint samples, and to support our plans to develop a transportable laboratory-based instrument capable of high resolution.

Throughout this article the term ‘non-invasive’ is intended to indicate that no material changes at all are made to the object under study. Although by no means universal, some authors have used ‘non-destructive’ to mean that the analytical technique in question does not *consume* the sample which is therefore subsequently available to other techniques, but not excluding the possibility that the sample has been prepared in some way prior to the measurement. For this reason, ‘non-invasive’ is the preferred term here.

Details of the experimental set-up and data processing are presented in Section 2 of this article. The results for six paints are highlighted in Section 3, illustrating the type of information that can be retrieved using the back-reflection EDXRD technique. The data for the remaining paint samples can be found in the Supplementary Information. In Section 4 we discuss the significance of these results and the complicating factors to be expected in the analysis of paintings as opposed to paint samples. We also highlight the prospects of transferring the technique into the laboratory and museum with comparable performance characteristics. Lastly, the conclusions of this study are presented in Section 5.

2. Materials and Methods

The data was acquired over two separate beamtime sessions on the B18 beamline [26] at the Diamond Light Source synchrotron in February 2019 and January 2020. The experimental configuration and the data preparation methods were based on the principles described in Hansford *et al* [25] but with some differences in the details, as described below.

2.1. Artists’ Paints

A pre-existing test panel with 41 oil-based paints commonly used by 20th century artists provided a representative range of pigment types. A full description of the paints is given by Polak *et al* [8] and additional details are given in the Supplementary Information. Diffraction data was acquired for each paint on the panel except Barite White (in this article the suppliers’ paint names have been capitalised) which showed clear signs of degradation. The paints have been applied generously with significant non-planar morphology of up to 5 mm relative to the panel surface. Summary information for each paint is shown in Table 1.

2.2. Experimental Configuration

The optimum implementation of the back-reflection EDXRD method requires an annular detector, with the incident beam passing through a central aperture, because this geometry simultaneously maximises both the 2θ angle and the detector area. PNDetector’s Rococo-2 four-channel silicon drift detector (SDD) assembly provides an excellent approximation to an annular design. The Rococo-2 has an active

Table 1. Summary of the artists' paints including phases identified in this work.

Paint Name	Supplier	Phases Identified	Group Assignment ^a
February 2019			
Aureolin	Michael Harding	K ₃ [Co(NO ₂) ₆]	A
Cadmium Gold Yellow	Michael Harding	CdS (greenockite)	A
Cadmium Red	Michael Harding	CdS _{1-x} Se _x	A
Cerulean Blue	Michael Harding	Co(Cr _x Al _{1-x}) ₂ O ₄ Al ₂ O ₃ (corundum) BaSO ₄ (barite)	A
Chrome Green	Rublev Colours	PbCr _{1-x} S _x O ₄	A
Chrome Yellow	Rublev Colours	PbCrO ₄ (crocoite) BaSO ₄ (barite)	A
Dioxazine Violet	BLOCKX	CaCO ₃ (calcite)	B
Flake White	Michael Harding	2PbCO ₃ •Pb(OH) ₂ (hydrocerussite) PbCO ₃ (cerussite) ZnO (zincite)	A
Flemish White	Rublev Colours	(PbO) ₃ PbSO ₄ •H ₂ O	A
Ivory Black	Michael Harding	Ca ₅ (PO ₄) ₃ OH (hydroxyapatite) CaCO ₃ (calcite)	A
Magenta	Michael Harding	-	D
Manganese Violet	Michael Harding	α,β- NH ₄ MnP ₂ O ₇	A
Minium	Rublev Colours	Pb ₃ O ₄ (minium)	A
Phthalocyanine Blue Lake	Michael Harding	-	D
Raw Sienna	Michael Harding	α-FeOOH (goethite) SiO ₂ (quartz) TiO ₂ (rutile)	A
Raw Umber	Michael Harding	α-FeOOH (goethite) SiO ₂ (quartz)	A
Scarlet Lake	Michael Harding	-	D
Terre Vert	Michael Harding	-	C
Ultramarine Blue	Michael Harding	(Na,Ca) ₈ [(S,Cl,SO ₄ ,OH) ₂ [Al ₆ Si ₆ O ₂₄]] (lazurite)	A
Vermilion	Rublev Colours	HgS (cinnabar)	A
Viridian	BLOCKX	-	C
Zinc White	Michael Harding	ZnO (zincite)	A
January 2020			
Alizarin Crimson	Michael Harding	-	D
Bright Yellow Lake	Michael Harding	TiO ₂ (rutile)	B
Chrome Oxide Green	Michael Harding	Cr ₂ O ₃ (eskolaite)	A
Cobalt Blue	Michael Harding	CoAl ₂ O ₄ (spinel group) Al ₂ O ₃ (corundum)	A
Cobalt Turquoise	Michael Harding	CoCr ₂ O ₄ (spinel group) Cr ₂ O ₃ (eskolaite)	A
Cremnitz White	Michael Harding	2PbCO ₃ •Pb(OH) ₂ (hydrocerussite) PbCO ₃ (cerussite)	A
French Yellow Ochre	Michael Harding	α-FeOOH (goethite) SiO ₂ (quartz) TiO ₂ (rutile)	A
Lamp Black	Michael Harding	-	D
Lemon Yellow	Michael Harding	BaCrO ₄	A
Manganese Blue	BLOCKX	ZnO (zincite)	B
Naples Yellow	Michael Harding	Pb ₂ Sb ₂ O ₇ (bindheimite) Pb ₂ SbSnO _{6.5} BaSO ₄ (barite)	A
Naphthol Red	Michael Harding	-	D
Orange Molybdate	Rublev Colours	-	C
Phthalocyanine Green Lake	Michael Harding	-	D
Pyrrolo Vermilion	BLOCKX	TiO ₂ (rutile) CaCO ₃ (calcite)	B
Titanium White #3	Michael Harding	TiO ₂ (rutile)	A
Transparent Red Oxide	Michael Harding	Fe ₂ O ₃ (hematite)	A
Yellow Lake	Michael Harding	-	D

^aSee Section 3 for the group definitions.

area of 60 mm² and a central aperture of 1.8 mm diameter. The detector assembly was mounted in a purpose-designed vacuum chamber that was incorporated onto the B18 beamline. To allow the greatest flexibility in the size, positioning and translation of samples, the experiment was designed so that objects of interest are mounted in free-space. The chamber therefore has a thin vacuum window mounted at the end of a small ‘snout’ and samples should ideally be placed within a few millimetres of the window in order to minimise X-ray absorption within the air gap. For many samples it was possible to achieve a 2 – 3 mm gap and 5 mm is considered the worst case in practice. For a 5 mm gap, the sample-detector distance is 155 mm, a considerable improvement on the previous configuration [25]. When combined with the larger detector area, the solid angle subtended by the detector has been increased six-fold. A photograph of the experimental configuration is shown in Fig. S2.

The use of a multi-element SDD brings an important advantage relative to a single SDD. Equal diffraction peak intensities on all four channels of the Rococo-2 is a reliable indicator of good powder averaging. Conversely, samples with large crystallites exhibit poor powder averaging with essentially random peak intensities – peaks can be completely missing on one or more detectors but present on others. Intermediate behaviour is also observed with the same peaks seen on all channels but with variable intensity. It is not unusual for one phase in a sample to show good powder averaging while another exhibits poor averaging (see, for example, Fig. S7), and indeed this result can potentially provide a means to assign peaks to one or other of the phases. These behaviours can provide valuable insights into the sample and phase characteristics.

The scan range of nominal X-ray energies for the results presented here was 2.1 – 5.1 keV, corresponding to $d = 2.95 - 1.22$ Å. For some of the paint samples in the earlier beamtime session, the scan range was reduced to 2.7 ($d = 2.30$ Å) to 5.1 keV because of a loss of signal at lower energies, probably due to a minor air leak into a sealed section of the beamline. The time taken to complete each scan was about 20 mins. As in previous work [25], the beam was defocused to approximately 1.7×0.9 mm² in order to maximise powder averaging. The variation of the height of the sample surface within this area is likely to be below 1 mm for all the paints. The typical flux at the sample on B18 is $\sim 5 \times 10^{11}$ photons s⁻¹ at 8 keV, with smaller values towards lower X-ray energies.

There was no visual indication of any radiation damage to the paints in these experiments. No additional tests were carried out to check for damage. Total radiation doses have been estimated using the equation given by Bertrand *et al* [27] (Table 1) and are around or below 5 MGy in all cases. Defocusing the beam is highly beneficial in reducing the potential for radiation damage. There have been only a small number of detailed studies of synchrotron radiation damage of pigments but the results have shown a damage threshold of ~ 10 MGy for chrome yellow [28] (worst case) and ‘10% level of damage’ for ultramarine of 7.7 MGy [29]. Consequently, the risk of radiation damage in the experiments reported here is minimal.

2.2.1. February 2019 beamtime

For this beamtime, the vacuum window was a nominally 3 µm thick carbon foil provided by Nannotek (Micromatter Technologies Inc.). The calculated total attenuation of a diffracted X-ray beam for a double-pass through this window plus a 5 mm air gap is shown in Fig. 1. The foil introduces a broad, relatively intense peak centred at 3691 eV corresponding to $d = 1.680$ Å while no other features attributable to the foil appear in the diffraction patterns. It is surmised that the foil has a graphitic structure with highly-oriented basal planes parallel to the foil surface. The observed feature corresponds to the (004) diffraction peak of graphite while no other allowed basal plane reflections occur within the scanned energy range [30].

Alignment of the Rococo-2 assembly with the synchrotron beam was a difficult process involving manual manipulation of the position of the detector head. Unfortunately, it was subsequently found that three of the four individual SDD elements had suffered varying degrees of damage, most likely caused by micro-cracking induced by mechanical stresses during manipulation [Andreas Liebel (PNDetector), personal communication, 2019]. The data reported here was recorded by the unaffected detector, though one other detector yielded data of sufficient quality to allow the degree of powder averaging in each diffraction pattern to be assessed.

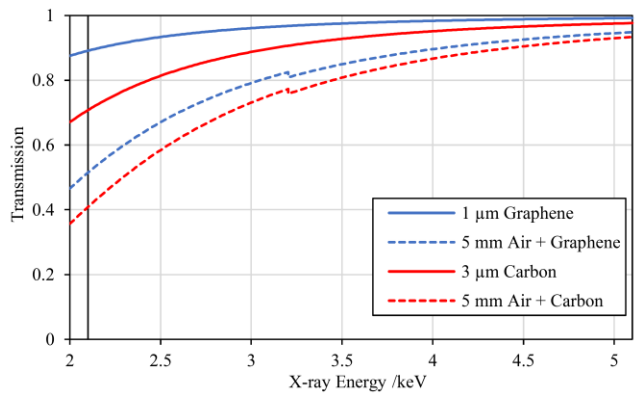


Fig. 1. Total X-ray attenuation for a double-pass through each X-ray window with and without a 5 mm air gap to the sample. The solid vertical line marks 2.1 keV, the lowest energy accessed in this work.

2.2.2. January 2020 beamtime

The damaged Rococo-2 assembly was replaced with an updated version incorporating xyz-translation stages, effectively solving the alignment difficulties and eliminating the risk of mechanical damage. The data from all four detector elements was of good quality, improving the overall signal-to-noise ratio and allowing good assessment of powder averaging, and the four channels were summed prior to analysis. Additionally, the 3 μm carbon foil window was replaced with a 1 μm graphene window supplied by Ketek GmbH [31]. The X-ray attenuation data for this window is shown in Fig. 1, illustrating that attenuation by the window itself now makes only a minor contribution to the total attenuation over the X-ray energies available on B18. Furthermore, the graphene window produces a much weaker and very broad graphitic (004) diffraction peak relative to the carbon foil window, centred at 3620 eV. In one further change, the 2.1 – 5.1 keV scan range was divided into two separate scans, joining at 2.8 keV, in order to bypass a Diamond data acquisition software limitation and increase the number of data points within each diffraction pattern and so avoid a larger-than-optimum step size across individual diffraction peaks.

2.3. Data Preparation

The preparation of the raw data generally followed the steps described previously [25]. TOPAS-Academic [32] was used for all crystallographic analysis of the diffraction patterns. The baseline-fitting capabilities of TOPAS were utilised instead of subtracting the baseline by fitting polynomial functions which can be a time-consuming process.

In order to obtain accurate d -spacings, it is vital to calibrate the nominal energy scale of the diffraction patterns. On B18, a Si double-crystal monochromator (DCM) was used to select a narrow X-ray energy bandpass utilising Si(111) diffraction [26]. The X-ray energy transmitted is dependent on the DCM angle according to the Bragg equation expressed in the energy domain:

$$E = \frac{hc}{2d_{\text{Si}(111)}\sin\theta_{\text{DCM}}} \quad (1)$$

where E is the X-ray energy, h is the Planck constant, c is the speed of light, $d_{\text{Si}(111)}$ is the d -spacing of the Si(111) reflection (taken to be 3.135693 Å [33]) and θ_{DCM} is the angle of the DCM relative to the incident beam. There can be a significant offset between the nominal DCM angle and the true angle which must be calibrated using diffraction standards.

2.3.1. February 2019 beamtime

A first, rough energy calibration was obtained by aligning the Ca K-edge XAFS spectrum from a marble sample with literature data for calcite [34]. In this step, the nominal DCM angle was shifted by -0.222° (the sign convention is defined below), to correct the energy scale to within ~ 1 eV. In addition, the experimental 2θ angle was estimated to be 178° , based on the dimensions of the experimental components. A more accurate calibration was then carried out by Le Bail fits to the diffraction patterns of the National Institute of Standards and Technology (NIST) powder diffraction standard reference materials (SRMs) 640e (Si powder) [33] and 660c (LaB₆ powder) [35] in energy-space in TOPAS. The approximate DCM offset and 2θ angles were used as a starting point for the refinements. Lattice parameters were fixed at the NIST-certified values, and the θ shift ($\delta\theta$) and DCM angle shift ($\delta\theta_{\text{DCM}}$) relative to the nominal values were optimised so that the calculated diffraction pattern best fitted the data, based on the relationship derived from the Bragg equation:

$$d_{\text{SRM}} = \frac{d_{\text{Si}(111)} \sin(\theta_{\text{DCM}} + \delta\theta_{\text{DCM}})}{\sin(\theta + \delta\theta)} \quad (2)$$

where d_{SRM} is the d -spacing of each reflection of the diffraction standard. Fits to three EDXRD spectra (two acquired at the start of the beamtime and one towards the end) from the LaB₆ powder and two spectra from the Si powder were performed to obtain five values for $\delta\theta$ and $\delta\theta_{\text{DCM}}$ to ensure reproducibility (see Fig. S3). The refined values were averaged to give a final $\delta\theta_{\text{DCM}}$ of -0.2152 (2°) and $\delta(2\theta) = 2\delta\theta = -0.63$ (3°), yielding $2\theta = 177.37$ (3°). No statistically significant difference in the DCM or 2θ angles was observed in spectra from the SRMs between the start and end of the experiment.

2.3.2. January 2020 beamtime

The same calibration procedure was followed for the more recent data except that there was no need for an initial rough calibration. Two EDXRD spectra of the LaB₆ powder (one acquired at the start and one towards the end) were fitted to yield $\delta\theta_{\text{DCM}} = -0.006853$ (7°). When $\delta\theta$ was included in the fits it was highly correlated with $\delta\theta_{\text{DCM}}$ and made virtually no difference to the weighted-profile reliability factor R_{wp} ; it was therefore fixed at zero without compromise to the accuracy of the calibration.

2.4. XRD Analysis

For simplicity within TOPAS and easier comparison with conventional XRD data, diffraction patterns were converted from energy-space to pseudo-angular-dispersive datasets using a dummy wavelength of 1.5406 \AA (corresponding to Cu K α_1 , 8.0478 keV). Subsequent references to the 2θ angle alludes to the converted data rather than a physical angle. Where available, information from the paint supplier and data from previous characterisation of the paint samples (Raman spectroscopy and elemental analysis [8]) were used to determine the phases likely to be present. Literature crystal structures for these phases were obtained from the Inorganic Crystal Structure Database (ICSD) [36] and used as structure models in TOPAS fits to the data. All diffraction peaks were fitted using the modified Thompson-Cox-Hastings pseudo-Voigt (TCHZ) peak shape [37]. The broad (004) graphite diffraction peaks attributed to the vacuum windows were handled by fitting either one or two (January 2020 or February 2019 data respectively) pseudo-Voigt peaks independently of the sample phases.

2.4.1. Crystallite Size Analysis

Fits to the diffraction data of the NIST LaB₆ SRM and two ZnO powder SRMs with certified median crystalline domain diameters of 60 nm and 15 nm (SRM 1979 [38]) were used to validate the accuracy of the crystallite size analysis based on peak broadening. A Pawley fit to the LaB₆ diffraction pattern was used to determine the instrument broadening as a function of 2θ , using the formulation specified

by Thompson-Cox-Hastings [37]. The instrument- and sample-broadening functions were then convoluted to analyse the ZnO data using a Pawley fit. The Scherrer equation allows the volume-weighted mean crystalline domain diameter, L_{vol} (which can differ significantly from the median, depending on the size distribution [39]), to be obtained from the sample-broadening function, giving values of 109 (13) nm and 22 (2) nm for the ‘60 nm’ and ‘15 nm’ samples respectively. The L_{vol} values reported in the NIST Certificate of Analysis [38], measured using two different diffractometers, are 138.9 (6) nm and 97.2 (14) nm for the ‘60 nm’ sample and 31.39 (9) nm and 31.7 (5) nm for the ‘15 nm’ sample. The level of consistency with the NIST values is considered sufficient for the purposes of this study. The crystalline domain diameters given in this paper are all volume-weighted except as noted below.

The crystallite shape model of Ectors *et al* [40] was fitted to a small number of phases with anisotropic peak broadening. In each of these cases the phase has trigonal symmetry (indexed using hexagonal coordinates) and a cylindrical crystallite shape was assumed with diameter L_x and length L_z . The cylinder axis is parallel to the $\langle 001 \rangle$ direction. The Ectors model provides area-weighted crystallite dimensions.

2.4.2. Phase Fraction Analysis

It is well known that quantitative phase analysis using EDXRD data is challenging because the dependence of the relevant physical quantities on X-ray energy are often not accurately known and may be difficult to calibrate [41]. The paint samples typically consist of crystalline pigments and fillers in an amorphous dried oil matrix in unknown relative amounts and the absorption coefficient cannot therefore be calculated *a priori*. The air gap between the vacuum window and the sample is also ill-constrained, affecting absorption at lower energies in particular. For some paint samples there are also sharp changes in the absorption coefficient at elemental absorption edges. Consequently, relative peak intensities contain poorly-defined experimental contributions as a function of energy that may be significant relative to the contribution of the diffracting phases.

Despite these difficulties, it has been found that Rietveld fits of acceptable quality can be achieved by including a scaling factor of the form $a\theta^b$ where a and b are refined parameters. This approach was validated using the NIST Si_3N_4 SRM 656 for quantitative phase analysis [42] (see Section S3). For samples that have absorption edges lying within the scanned energy range, the data was divided into segments with each segment having an independent scaling factor of the form described above. Absorption edges are manifested most obviously as sudden jumps in the baseline [25], but in many cases these jumps are very small (e.g. the Ar K-edge at 3206 eV) or not observed at all. In such cases the effect on diffraction peak intensities is negligible and can be ignored. To minimise the number of refined variables, crystallographic parameters affecting intensity (i.e. atomic co-ordinates, site occupancy and atomic displacement parameters) were fixed using published structures. In some cases there were no published displacement parameters in which case generic isotropic values were chosen. Where multiple structures were available, the one with lattice parameters most closely matching the values obtained from the initial Pawley fit was selected. Preferred orientation parameters can also be included in the Rietveld refinements if required.

3. Results

The results of the XRD analyses of the 40 paint diffraction patterns have been categorised into four groups:

- A. Paints for which at least one pigment phase has been identified and, as a minimum, unit cell parameters have been derived.

- B. Paints for which only phase(s) other than the pigment has/have been identified (and unit cell parameters derived). Phases such as calcite and barite are commonly used as fillers or extenders.
- C. Paints that have clearly identifiable peaks in their diffraction patterns and sufficiently good powder averaging (see below) but incomplete or unsatisfactory analyses. It is possible that these patterns can be analysed if correct phase identifications can be made.
- D. The remaining paints have patterns either devoid of any diffraction features at all or have low quality patterns that are not amenable to meaningful analysis.

The number of paints falling into each category are, respectively: 25, four, three and eight, although deciding whether a paint belongs in Group C or D is not always straightforward (see Sections S7.3 and S7.4). Of the eight paints in group D, seven contain synthetic organic pigments. Indeed, no organic pigments have been identified by their diffraction patterns in this work. The results of the analyses are summarised in Table 1.

In total, two of the paints with inorganic pigments produced poor diffraction patterns. The data acquired for the Lamp Black paint is completely devoid of diffraction peaks (Fig. S37h), an unsurprising result given that many carbon-based blacks are amorphous or poorly crystalline [6]. The diffraction pattern of the Viridian paint (pigment: hydrated chromium oxide, $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) shows very broad peaks (Fig. S36b), consistent with previous studies [43, 44]. Furthermore, the authors could find no published crystal structure for $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ and it appears that this hydrated oxide is inherently poorly crystalline at best. All of the remaining paints with inorganic pigments have relatively good quality diffraction patterns (groups A and C).

As mentioned in Section 2.2, the degree of powder averaging can be qualitatively assessed by comparing the data from the available detector channels. The majority of the paints show ‘moderately good’ powder averaging, defined as the observation of the same peaks in the available channels but with varying intensities. A minority of paints have excellent powder averaging with essentially identical peak intensities in all channels (e.g. Fig. S5). The occurrence of peaks appearing in one channel only is observed for perhaps just two or three paints (e.g. Fig. S7); even in these cases there are other phases present with good powder averaging. The main consequence of less than ideal powder averaging is expected to be reduced accuracy in quantitative phase analysis. The observation of reasonably good powder averaging despite the small volume of paint probed by the X-ray beam is perhaps unsurprising given that essentially all paints are prepared by mixing pigments in powdered form with a binding agent.

The crystallographic analyses of several paint samples are highlighted in the sub-sections below, demonstrating the range of information that can be retrieved using the back-reflection EDXRD technique. The data and analyses for all the remaining paints are presented in the Supplementary Information.

3.1. Cadmium Gold Yellow and Cadmium Red

The pigments in the Cadmium Gold Yellow and Cadmium Red paints are cadmium sulphide (CdS) and cadmium sulphide selenide ($\text{CdS}_{1-x}\text{Se}_x$) respectively. CdS can exist in two polymorphic forms: the zinc blende ($F4\bar{3}m$) and the wurtzite ($P6_3mc$) structures, the latter of which is more commonly used in paints thanks to its brighter colour and higher thermal stability [45]. For the solid solution $\text{CdS}_{1-x}\text{Se}_x$, the full composition range with the wurtzite structure is possible and the shade of red is dependent on the degree of Se substitution [45]. Cadmium yellow is known to degrade in historical paintings, an area of active research [46]. The consensus is that CdS nano-crystallites are more prone to degradation relative to larger crystallites. XRD analysis therefore has a potential role in degradation studies through the identification of crystalline microstructure.

Pawley fits to both diffraction patterns using the wurtzite structure, Fig. 2 (a) and (b), account for all of the observed peaks and the results are reported in Table 2. To determine the Se substitution value for Cadmium Red, literature values for the lattice parameters of wurtzite-type CdS [47], CdSe [48] and intermediate compositions [49-51] were used to calculate the unit cell volume to generate a single metric for comparison. A plot of the unit cell volume as a function of x , Fig. 2 (c), shows a near-Vegard's law relationship, yielding $x = 0.36$ (3) for the phase in the Cadmium Red paint sample. It is assumed that no other elements are involved in the solid solution.

The diffraction peak widths and profile shapes show some interesting behaviour. The (103) and (203) reflections, and only these two, have 'super-Lorentzian' lineshapes, while the adjacent (210) and (211) peaks have asymmetric profiles with significant intensity appearing between these peaks. These distinct features are present in both diffraction patterns but to a lesser extent in the Cadmium Red pattern. In addition, the (110) peak is moderately asymmetric in the Cadmium Gold Yellow pattern only. Previous studies of CdS nanoparticles have commonly found that the (103) peak is especially broad [52-55]. The anisotropy in the peak widths as a function of hkl as exhibited by the Cd pigments is characteristic of stacking faults which are commonly found in hexagonal crystal structures [56]. Warren [57] has shown that reflections with $h - k = 3n$ (where n is an integer) are unaffected and remain sharp whereas other reflections are broadened as a consequence of stacking faults, proportional to both the fault density and the magnitude of l . Quantitative analysis of the microstructure of these pigments is beyond the scope of this study.

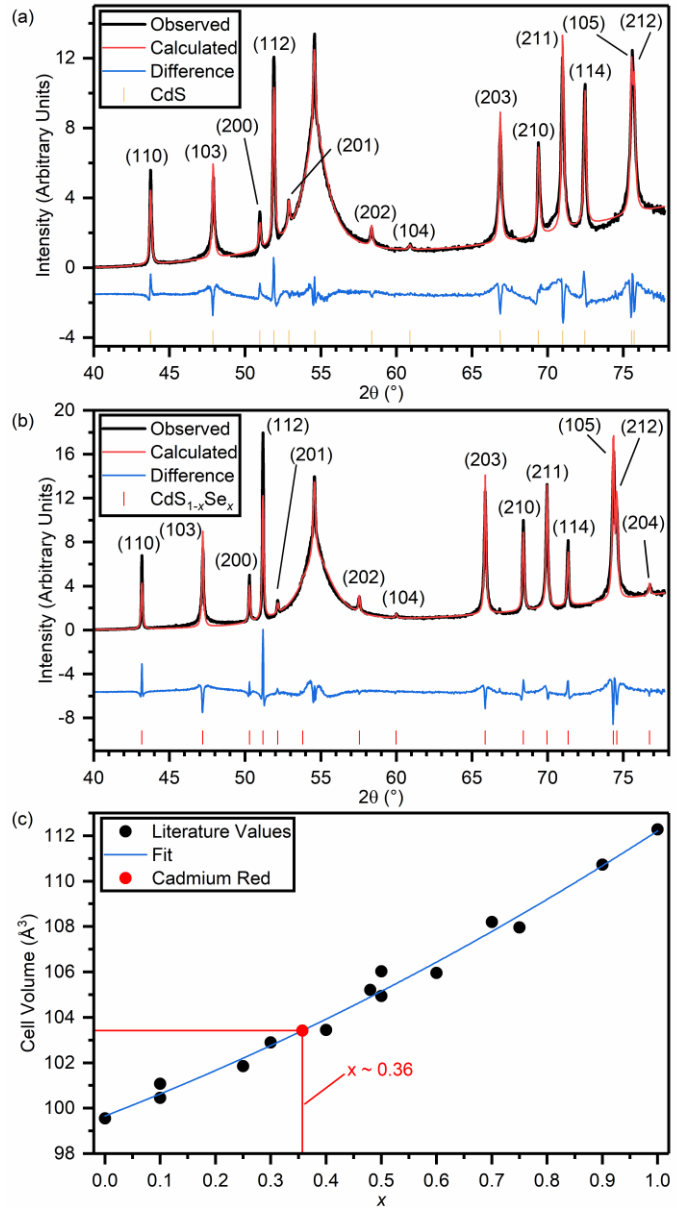


Fig. 2. Pawley fits to the (a) Cadmium Gold Yellow and (b) Cadmium Red diffraction patterns. The broad peak centred on $2\theta = 54.8^\circ$ is due to diffraction by the graphitic vacuum window, and was fitted by inclusion of two pseudo-Voigt functions. The difference plots are shown offset on the vertical scales. (c) Plot of the unit cell volume of $\text{CdS}_{1-x}\text{Se}_x$ solid solutions vs x from literature data with a quadratic fit, together with an estimate of x for Cadmium Red.

Table 2. Crystallographic parameters of the identified phases in the Cadmium Gold Yellow and Cadmium Red paints.

Phase	Sowa [47]	Pawley Fit
CdS ($P6_3mc$)		
a (Å)	4.1365 (3)	4.13435 (7)
c (Å)	6.7160 (4)	6.7159 (2)
R_{wp} %		11.6
CdS_{1-x}Se_x ($P6_3mc$)		
a (Å)		4.18758 (6)
c (Å)		6.81004 (14)
x^a		0.36 (3)
R_{wp} %		17.0

^aThis parameter was not derived in the Pawley fit; see main text for details.

3.2. Manganese Violet

The pigment in Manganese Violet is a manganese complex, $\text{NH}_4\text{MnP}_2\text{O}_7$, and two polymorphs have previously been demonstrated to be present in commercial paint samples [58, 59]. Past work with non-invasive portable XRD has struggled to assign peaks in Manganese Violet samples due to the complex diffraction pattern and the limited resolution and d -space range afforded by the instrument [59]. The resolution of the back-reflection EDXRD experimental technique yields a high-quality diffraction pattern from the Manganese Violet paint, to which a two-phase Pawley fit gives excellent agreement. It has been assumed that the broadening of peaks due to the sample, beyond instrument broadening, is caused by small crystallite domain sizes. On this basis, the volume-weighted mean crystallite diameters of the α - and β -polymorphs are 102 (3) nm and 480 (40) nm respectively. The relatively large crystallite size, and the large error, derived for the β -polymorph should be interpreted in the context of the limit of applicability of the Scherrer equation that is generally on the order of 100 – 200 nm [60, 61]. The refined lattice parameters of both polymorphs (Table 3) are close to published values [58], supporting the use of the published crystal structures in the subsequent Rietveld fit. The phase weight fractions are the same within errors to the values obtained by Begum and Wright [58] even though the paint they analysed came from a different supplier, possibly suggesting that both paint suppliers procured the pigment from the same manufacturer. It is notable that these authors were not able to synthesise the β -polymorph in isolation.

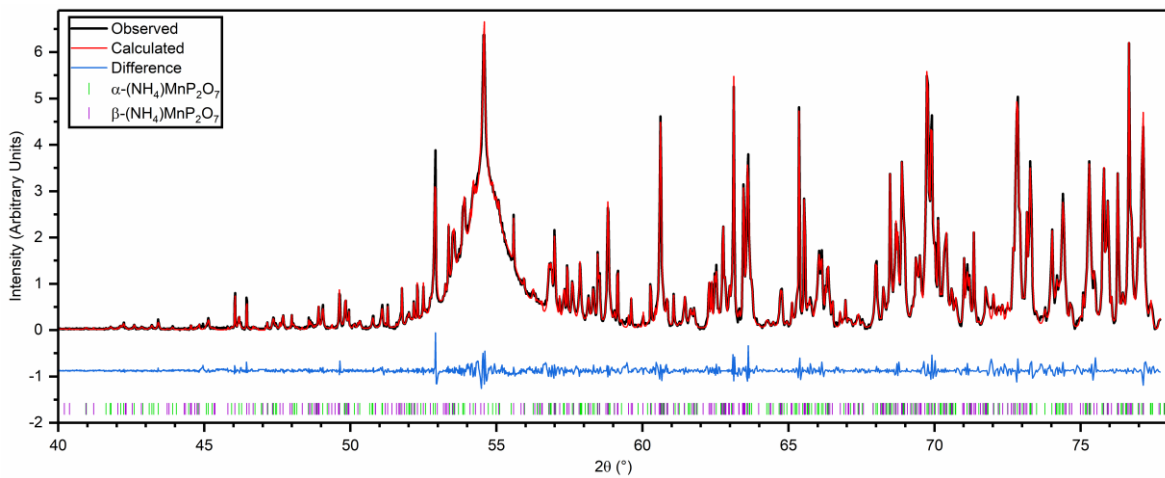


Fig. 3. Pawley fit to the Manganese Violet diffraction pattern. The broad peak centred on $2\theta = 54.8^\circ$ is due to diffraction by the graphitic vacuum window, and was fitted by inclusion of two pseudo-Voigt functions. The difference plot is shown offset on the vertical scale.

Table 3. Crystallographic parameters of the identified phases in the Manganese Violet paint.

Phase	Begum and Wright [58]	This work
α-NH₄MnP₂O₇ ($P2_1/c$)		
<i>a</i> (Å)	7.4252 (3)	7.4150 (2)
<i>b</i> (Å)	9.6990 (4)	9.7047 (3)
<i>c</i> (Å)	8.6552 (4)	8.6451 (3)
β (°)	105.627 (3)	105.551 (2)
Weight fraction ^a (%)	69 (3)	71 (2)
Mean crystallite size (nm)		102 (3)
β-NH₄MnP₂O₇ ($P\bar{1}$)		
<i>a</i> (Å)	8.4034 (6)	8.40359 (14)
<i>b</i> (Å)	6.1498 (4)	6.14997 (5)
<i>c</i> (Å)	6.1071 (4)	6.10641 (6)
α (°)	104.618 (5)	104.6288 (11)
β (°)	100.748 (5)	100.7411 (10)
γ (°)	96.802 (6)	96.8044 (11)
Weight fraction ^a (%)	31 (3)	29 (2)
Mean crystallite size (nm)		480 (40)
R_{wp} (%) (Pawley/Rietveld)		11.3/33.1

^aDerived from the Rietveld refinement; all other parameters are from the Pawley fit.

3.3. Flake White and Cremnitz White

Lead white is a pigment widely used since antiquity and well into the 20th century despite the advent of cheaper and safer whites, the oxides of zinc and titanium, developed in the 19th and 20th centuries respectively [6]. Lead white can contain a range of lead carbonate compounds [6], usually dominated by lead carbonate hydroxide [2PbCO₃•Pb(OH)₂, hydrocerussite] and lead carbonate (PbCO₃, cerussite). The ratio of these two phases, and their crystallite sizes, shapes and preferred orientation, can affect the optical properties of the paint, as well as being indicative of synthesis method and painters' techniques [5, 62-67]. Powder XRD analysis offers the most powerful method to distinguish the lead carbonates and elucidate their structural properties in paints.

The Flake White and Cremnitz White paints analysed in this study are both based on lead white. Both contain cerussite and hydrocerussite while Flake White also contains ZnO. The unit cell parameters of each phase were derived from Pawley fits to the data and are close to literature values (Table 4). A series of Pawley fits were also used to investigate the microstructure of the phases. Hydrocerussite commonly occurs as platy crystallites [65] and the observed anisotropic peak broadening was fitted using the crystallite shape model of Ectors *et al* [40] assuming a cylindrical shape. The results suggest that the hydrocerussite crystallites in Cremnitz White are significantly more anisotropic in shape than in Flake White (Table 4). It should be noted that trial Pawley fits using the Stephens anisotropic strain model [68] gave comparable R_{wp} values, and the presence of microstrain in the hydrocerussite phases (with or without size effects) cannot be ruled out based on these results.

Attempts to fit the anisotropic shape model to the cerussite phases gave unconvincing results and isotropic shapes were assumed in the final Pawley fits. In both paints the cerussite phase exhibits poor powder averaging, relative to the hydrocerussite and ZnO phases, and in some instances the peak shapes are irregular, suggesting the influence of larger, individual crystallites. For this reason, the crystallite sizes derived for the cerussite phases are not considered reliable and this parameter has only been included in the refinements to improve the overall fit. An anisotropic shape model was also not

supported for the ZnO phase in Flake White. Rietveld refinements were performed using published crystal structures (as reported in Table 4) in order to derive phase ratio quantifications. The hydrocerussite phase in both paints shows preferred orientation in the $\langle 001 \rangle$ direction, as expected for the platy crystallites. The degree of preferred orientation is significantly greater for Cremnitz White, consistent with the more pronounced shape anisotropy. For Flake White, introducing the single preferred orientation parameter, r , of the March-Dollase model [69] gave an adequate fit with most of the discrepancy between the fit and the data arising from the poor powder averaging of the cerussite phase, Fig. 4(b). A corresponding fit to Cremnitz White gives a much lower value of r (Table 4), indicative of greater preferred orientation, but the R_{wp} factor is relatively high and there remain significant errors in the fit to the hydrocerussite peak intensities. Instead, an eight-term spherical harmonic [70] was used to model the hydrocerussite preferred orientation. The remaining discrepancies are again primarily due to cerussite poor powder averaging. The latter factor undoubtedly limits the accuracy of the quantification (see Section S6). In both paints, hydrocerussite is the dominant lead carbonate phase as commonly observed in Old Masters paintings [65], for example, and consistent with the stack manufacturing process [66].

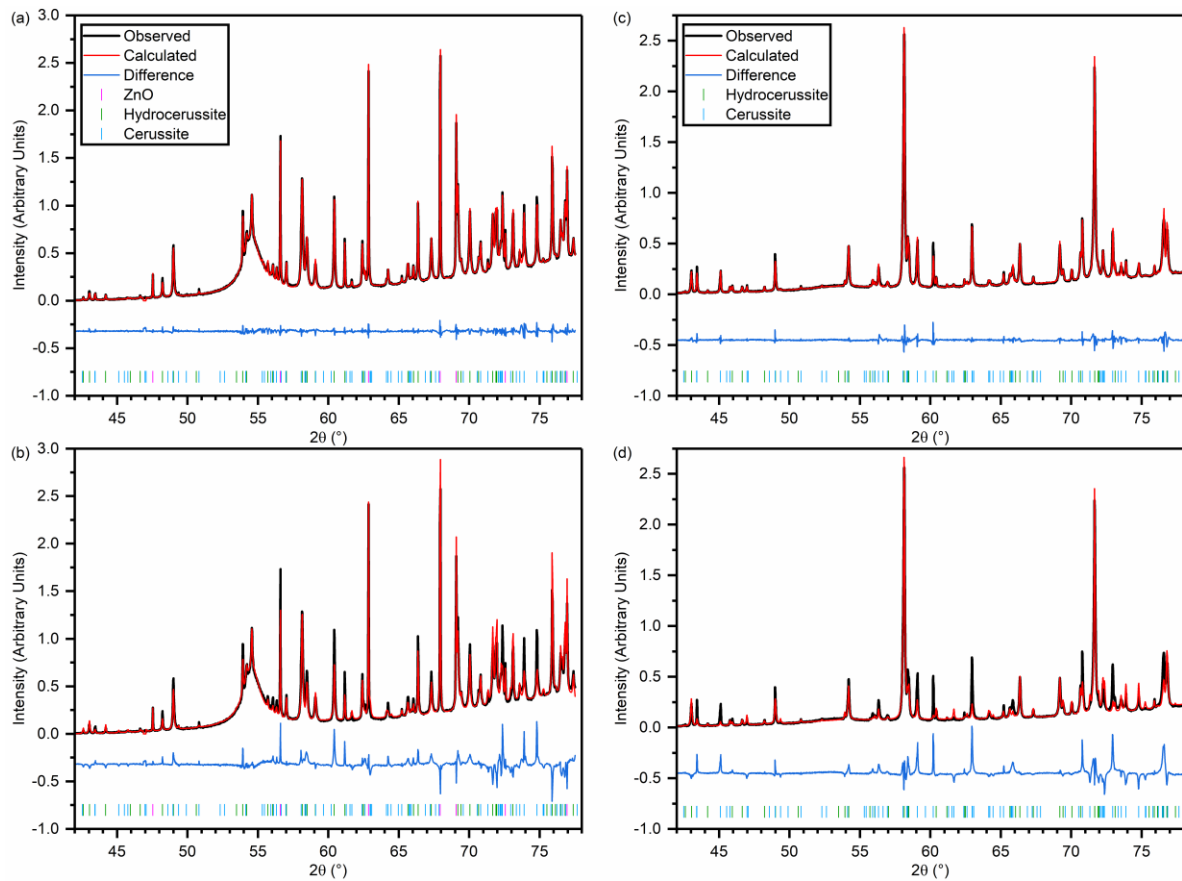


Fig. 4. (a) Pawley fit and (b) Rietveld refinement to the Flake White diffraction pattern. (c) Pawley fit and (d) Rietveld refinement to the Cremnitz White diffraction pattern. In each case the difference plot is shown offset on the vertical scale.

Table 4. Crystallographic parameters of the identified phases in the Flake White and Cremnitz White paints.

Phase	Literature	Flake White	Cremnitz White
2PbCO₃•Pb(OH)₂ (<i>R</i>$\bar{3}$<i>m</i>)	Siidra <i>et al</i> [71]		
<i>a</i> (Å)	5.2475 (1)	5.24405 (2)	5.24372 (6)
<i>c</i> (Å)	23.6795 (7)	23.6819 (2)	23.68405 (10)
<i>L_x</i> (nm)		136 (6)	230 (30)
<i>L_z</i> (nm)		32.6 (6)	32.8 (4)
<i>L_x/L_z</i>		4.2 (2)	7.0 (8)
Weight fraction ^a (%)		56.2 (10)	81.0 (8)
<i>r</i> (001) ^a		0.709 (6)	0.383 ^b (3)
PbCO₃ (<i>Pm</i><i>cn</i>)	Antao & Hassan [72]		
<i>a</i> (Å)	5.18324 (2)	5.18236 (13)	5.18265 (5)
<i>b</i> (Å)	8.49920 (3)	8.4968 (2)	8.50094 (9)
<i>c</i> (Å)	6.14746 (3)	6.1435 (2)	6.14231 (8)
Crystallite size (nm)		95 (2)	89 (2)
Weight fraction ^a (%)		10.9 (5)	19.0 (8)
HC/(HC + C) ^c (%)		83.8 (11)	81.0 (8)
ZnO (<i>P</i>$\bar{6}$<i>3mc</i>)	NIST [38]		
<i>a</i> (Å)	3.24983 (8)	3.249919 (9)	
<i>c</i> (Å)	5.2068 (1)	5.20682 (3)	
Weight fraction ^a (%)		32.9 (9)	
<i>R_{wp}</i> (%) (Pawley/Rietveld)		4.7/12.1	7.2/21.0

^aDerived from the Rietveld refinements; all other parameters are from the Pawley fits.

^bThis value is derived from a separate Rietveld refinement in order to have a value directly comparable with the Flake White result.

^cHC = hydrocerussite, C = cerussite.

3.4. Naples Yellow

Naples Yellow is commonly identified as lead antimonate (Pb₂Sb₂O₇) which has a cubic pyrochlore structure. There are several closely-related yellow lead-based mixed oxide pigments which have a complicated history in glass-making, ceramics and paintings, having been lost and rediscovered several times [73-75]. Remarkably, the occurrence of the lead tin antimonate phase Pb₂SbSnO_{6.5} in pre-20th century paintings was rediscovered as recently as 1998 [76, 77]. Furthermore, doubt has been cast on the existence of stoichiometric Pb₂Sb₂O₇ as a cubic phase in a recent study suggesting that partial substitution of Pb with Na is required for stabilisation [74]. Further art historical research into the relationship between the characteristics of these pigments and their temporal and geographical use offers considerable potential for authentication and provenancing purposes [73, 74].

The Naples Yellow pattern, Fig. 5, has several broad diffraction features (referred to here as ‘bands’) with relatively steep sides, behaviour that can be recognised as characteristic of a continuous series of phases within a solid solution [78]. The positions of these bands are consistent with cubic pyrochlore phases. A Pawley fit of the pattern shows that the end-members have lattice parameters of *a* = 10.39413 (6) Å and 10.56866 (8) Å, comparable to literature values for Pb₂Sb₂O₇ (10.40 Å [79]) and Pb₂SbSnO_{6.5} (10.5645 Å [80]). To adequately fit the intensity between the end-member phase peaks, a total of 12 additional pyrochlore phases were included with their lattice parameters constrained to spread evenly between the end-member values. This number of phases is required to model the steep sides of the diffraction bands and to capture the relatively sharp peaks within some of the bands. Barite (BaSO₄, *Pnma*) has also been identified and is included in the Pawley fit [unit cell parameters: *a* = 7.15335 (6) Å, *b* = 8.87463 (8) Å, *c* = 5.45266 (6) Å]. It is apparent from inspection of the data from the four SDD

channels that the powder averaging of this sample is relatively poor (Fig. S8) and a Rietveld refinement to quantify the phase ratios has not therefore been attempted.

Several previous XRD and Raman studies of lead antimonate pigments have observed bimodal compositions, both in artworks and in synthesised samples [73, 74, 81-83], though with lattice parameters that do not necessarily correspond to the stoichiometric end-members. In contrast to the data presented here, these studies appear to show a genuine bimodality rather than a continuous solid solution. This disparity is presumed to relate to differences in the pigment production methods.

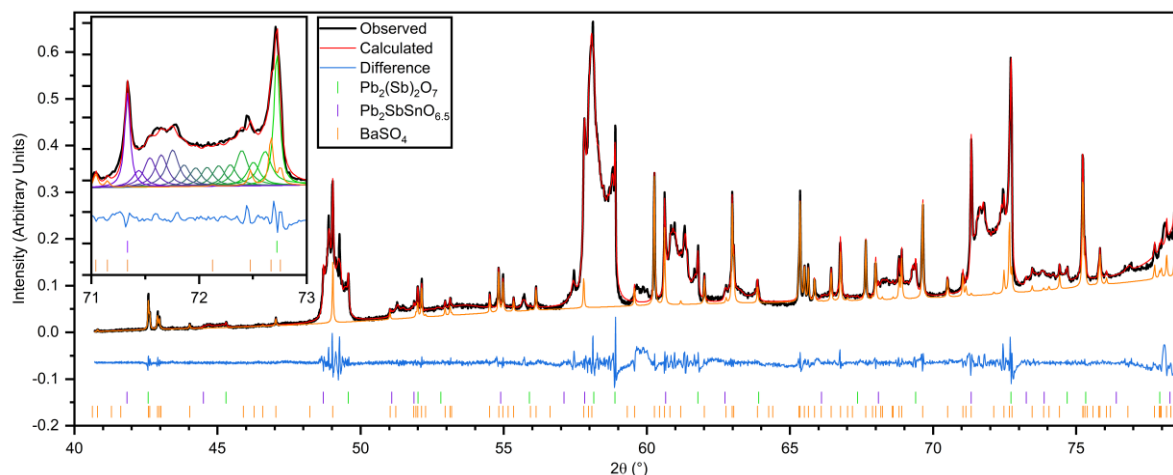


Fig. 5. Pawley fit to the Naples Yellow diffraction pattern. The fitted barite peaks are shown in orange. The inset shows an expansion of the $2\theta = 71^\circ - 73^\circ$ range with all of the fitted peaks due to the solid solution phases shown colour-coded. The difference plot is shown offset on the vertical scale.

4. Discussion

A significant outcome of this study is the lack of detection of any of the organic pigments, even those containing a heavy element such the copper phthalocyanine pigments. Some weak peaks are visible in some of the diffraction patterns of paints containing an organic pigment (see Fig. S37), but nothing that allows identification. Based on this work alone, it is not possible to determine whether the failure to detect organic pigments results from a lack of sensitivity or because they are poorly crystalline or amorphous.

Organic pigments typically have high tinting strength [84] and therefore constitute a small weight fraction of commercial paints. Organics are weak X-ray scatterers because of their low average atomic number and paints based on organic pigments frequently contain inorganic fillers and extenders [85]. (In principle, if the XRD characteristics of the inorganic components associated with a specific organic pigment are sufficiently distinct, and the association can be made unambiguously, the inorganics could act as tracer for the organic pigment. It seems likely that these criteria will rarely be met in practice however). The inorganic phases are much more efficient diffractors and produce patterns that may overlay the organic diffraction peaks. More importantly, they limit the penetration depth of X-rays into the paint by absorption and therefore significantly reduce the probed volume and hence the diffraction signal from the organic components. Furthermore, previous studies have shown that dry organic pigment powders typically produce clearly identifiable diffraction patterns only below $2\theta \approx 30^\circ$ (Cu-K α) [9, 84, 86], equivalent to $d = 3.0 \text{ \AA}$ or 2.1 keV in back-reflection EDXRD. As currently implemented, the back-reflection technique cannot access this range. All these factors, acting in concert, predict weak diffraction from organic pigments, perhaps below the limit of sensitivity in the present study. Additionally, the extent to which organic pigments retain crystallinity when prepared as paints is unclear. It is interesting to note that two earlier studies concluded that organic pigments are more

difficult to identify with XRD in oil-based paints compared to acrylic or alkyd binders, though it is not clear whether the primary factor is the more frequent presence of inorganic components [85] or poor crystallinity [9]. In future studies it will be interesting to see whether diffraction patterns can be observed for organic pigments in acrylic or alkyd media and whether larger d -spacing peaks can be detected when extending the method to lower energies (see below).

The current limitation on the observable d -spacing range can affect the analysis of inorganic paints also. Large d -spacing/low-angle diffraction peaks are highly diagnostic for phase identification [25] and the absence of these peaks in the data reported here can hinder identification. For most of the paints, the identity of the pigment and any extenders was either known in advance or could be restricted to a limited set of candidates. One exception is the Terre Vert paint (Fig. S36a) which contains the green earth pigment, described by the supplier as a complex of ferrous silicates in aluminium and magnesium clays. Green earth most commonly contains the natural green clay minerals glauconite and celadonite [6] but there are exceptions [87] and modern varieties may be adulterated with synthetic organic greens [88]. To date, the authors have been unable to find satisfactory identifications of the phases present in the Terre Vert paint.

The results of this study demonstrate the range of information about the paint samples that can be extracted using the back-reflection EDXRD technique, non-invasively and at high resolution: phase identification (including solid solutions), highly accurate unit cell parameters, quantification of the observed phases, crystallite size and strain parameters and preferred orientation parameters. The paints chosen for presentation in Section 3 highlight these capabilities. The high resolution of the method enables effective analysis even in cases of very high peak density such as the Manganese Violet paint which contains a pigment with two low-symmetry polymorphs. In all of the paint data acquired in this study, the widths of the diffraction peaks are limited by sample effects, not by instrumental broadening. Although Manganese Violet is not a particularly common pigment, the other pigments for which results are presented in Section 3 are all highly significant in art history and conservation and are the subjects of active research. For example, there is considerable interest in the microstructural properties of the lead white phases and how they relate to historical production methods [62, 64-67]. The analysis of microstructure by powder XRD is a very broad topic within the field, ranging from basic application of the Scherrer equation to modelling of the whole pattern using highly detailed physical models such as the work of Scardi and Leoni [89-91], and there is a concomitant requirement of time and effort to achieve meaningful results. In complex cases, depending on the aims of the study, the effort required for a detailed physically-based analysis may not be warranted. However, in such cases the observed pattern of diffraction peak widths and profile shapes can serve as a fingerprint that may be unique to a specific artist or supplier within a limited geographical region and timeframe. The cadmium pigments reported in Section 3.1 provide a good example. Once again, the high resolution of the back-reflection EDXRD technique is crucial in faithfully recording the characteristics of the diffraction pattern determined by the sample physical properties and not limited by instrumental effects.

In general terms, phase identification can contribute to art historical knowledge for artworks of known provenance, or aid attribution and authentication where provenance is in doubt. The distinction and quantification of polymorphs (e.g. Manganese Violet) and other closely-related phases (e.g. lead tin antimonates in Naples Yellow) allows the synthesis of more in-depth knowledge than pigment identification alone. As mentioned in connection with lead white, phase quantification along with crystallite size and shape information can distinguish alternative production methods [65] which, again, can either yield historical insights or serve to delimit the geotemporal production. There is also considerable potential to discern details of the artist's technique, whether through the choice of specific pigment variants [5] or the application of paint onto a canvas deduced by mapping preferred orientation

[92]. Although not demonstrated as part of this study, there is every reason to suppose that degradation phases can be detected using the back-reflection method, allowing elucidation of degradation mechanisms and informing the development of conservation and restoration strategies.

This study has focused on the analysis of individual paint samples and, clearly, real paintings will present additional challenges. The dilution and mixing of paints will reduce the diffraction signal from any one phase and yield more complex diffraction patterns. The high resolution of the technique is a major advantage in mitigating the challenge posed by complexity. The presence of amorphous varnish overlaying the paint will also attenuate the diffraction signal of the pigments. A possible way to mitigate this factor is to extend the method to higher X-ray energies to take advantage of their greater penetrating power (see Section S5). EDXRD patterns become more crowded at higher energies [23] but, again, high resolution is beneficial in this respect. It is possible that, with the appropriate calibrations, the thickness of a varnish layer could be estimated via the attenuation effect as a function of energy. In any case, the demonstrated performance of the back-reflection EDXRD technique presented here establishes a baseline of what is achievable in favourable cases. Additionally, it is possible in principle to retrieve the relative depths of the diffracting phases within the probed volume by assessing diffraction peak intensity ratios as a function of X-ray energy, as long as the phases show good powder averaging. In this way, it may be possible to distinguish paint layers.

The need to access synchrotron facilities is a disadvantage in cultural heritage studies because of the limited beamtime available and the need to transport valuable objects. It is possible to transfer the back-reflection technique into the laboratory with only a modest penalty in terms of resolution through the use of transition-edge sensor (TES) arrays [93-95], also known as microcalorimeters, a technology that has undergone rapid development in recent years. These devices are state-of-the-art X-ray detectors offering spectral resolutions on the order of a few eV, approaching two orders of magnitude improvement over the best solid state detectors [96]. The development of sensor arrays and advanced sensor design and signal processing methods allows detection rates in the 10s kilo-counts per second range, with greater capabilities expected in the future [94]. These rates are compatible with the requirements of back-reflection EDXRD using laboratory sources [23].

The use of microcalorimeters in a laboratory setting brings multiple advantages. The most significant advantage, relative to synchrotron implementation, is the simultaneous acquisition of the whole diffraction pattern. It is this factor that allows the use of a laboratory source despite the orders of magnitude reduction in brilliance, also reducing the risk of radiation damage. Implementation with microcalorimeters will also allow access to lower X-ray energies/larger d -spacings, subject to the limitations imposed by window and air absorption if samples are mounted in free-space. Where necessary, objects can be mounted within a bagged enclosure flushed with He. For objects or artworks that exhibit poor powder averaging, the deleterious effect on diffraction patterns can be mitigated by employing a larger beam spot; for example, a spot size of 10 mm will increase the probed volume by a factor of 100 relative to the ~1 mm spot size employed in the synchrotron experiments (assuming sample homogeneity). Further improvement is achievable via lateral scanning and/or sample tilting during data acquisition. For broadband detection the sample movement can be *slow*, whereas for the equivalent averaging effect at the synchrotron the same movement would have to be repeated at each step during scanning of the X-ray energy. One final advantage of microcalorimeters in this context will be the simultaneous acquisition of highly complementary XRF data, yielding elemental composition. The occurrence of XRF peaks in EDXRD is normally considered a disadvantage because of the potential for overlap [97], but with eV-scale resolution this factor becomes an advantage. It may even be possible in some instances to deduce chemical environment data from XRF data [95, 98], in support of phase identification through XRD analysis. The authors anticipate that a microcalorimeter-based instrument

will be transportable [Joseph Fowler, NIST, personal communication, 2019], allowing *in situ* investigations in museums and art galleries and access to artefacts that cannot be moved because of their bulk or prohibitive insurance costs.

On the basis of acquisition time per measurement spot of ~20 mins, 2D mapping [99] of a painting would take a prohibitively long time to record a meaningful dataset. If the primary aim was simply to identify the pigments present in the mapped area, the scan time per spot could be reduced significantly by scanning the monochromator more quickly and over a shorter energy range. It would be essential to ensure that the more intense, resolved diffraction peaks of pigments of interest are within the scanned range. Even with these changes, it is likely that measurement times would still need to be a few mins per spot whereas dwell time in the secs range are required for mapping applications [99]. When implemented using microcalorimeters, simulations suggest that acquisition times can be *shortened* relative to the synchrotron, though the improvement factor depends strongly on details of the experimental design such as the geometry and X-ray tube power. Insufficient work has been performed to date to assess potential acquisition times and whether mapping applications will be feasible. Longer total acquisition times can be tolerated for a laboratory instrument, favouring the possibility of mapping applications. Good spatial resolution can be achieved with the use of a focusing polycapillary optic [100] to give a small beam spot on the sample.

As with all analytical techniques, the back-reflection EDXRD method comes with a set of advantages and disadvantages. The key advantage, indeed the *raison d'être* of the method, is that it is extremely tolerant of the surface morphology of the sample [23,25]. It follows that there is also no need to position samples a precise distance relative to the instrument. These advantages hold true even when implemented at the very high resolution afforded at the synchrotron; samples can be moved several mm away from the instrument without significant consequence [25], an inconceivably large distance by the standards of conventional angle-dispersive XRD. Furthermore, we fully expect to be able to transfer the technique into the laboratory and museum using microcalorimeter technology with only a modest penalty in the achievable spectral resolution. The results of a direct comparison between synchrotron and laboratory data for two of the paints (Cobalt Blue and Cremnitz White) are shown in Section S6 to illustrate the superior resolution of the EDXRD data. High resolution enables the extraction of an extensive set of crystallographic parameters, including microstructure, contrasting with current portable XRD instrumentation (see sec. 1). A key part of our plans includes proof-of-principle experiments using microcalorimeters. An additional advantage of the method is the convenience of the inherent back-reflection geometry that minimises the potential for physical interference between the instrument and the object being studied.

One of the disadvantages of the technique is the difficulty in accessing low energies/large *d*-spacings. On beamline B18 at Diamond, there is a hard limit of 2.05 keV set by the Si(111) monochromator, but more generally absorption in air and by the vacuum window becomes a limiting factor at these soft X-ray energies. Quantitative phase analysis of EDXRD data is more challenging than for angle-dispersive methods because of the ill-constrained energy-dependence of absorption and other parameters, leading in general to reduced accuracy. Also, achieving high resolution requires either transportation of artefacts to a synchrotron facility or the use of expensive microcalorimeters. It is anticipated that an instrument based on microcalorimeters will be transportable, but certainly considerably bulkier than existing portable XRD equipment. Good powder averaging cannot be guaranteed for any specific sample, but this issue applies to all non-invasive XRD techniques.

In summary, we believe that the combination of non-invasive capability and uncompromised data quality through high spectral resolution distinguishes the back-reflection EDXRD technique from alternative non-invasive XRD methods.

5. Conclusions

The back-reflection EDXRD technique, implemented at high resolution, shows excellent potential for the analysis of inorganic pigments in paints. Of the 40 paints for which data was acquired, 29 are inorganic-based and successful analysis was possible for 25 of these (86%), where success is defined as phase identification and retrieval of the unit cell parameters of the pigment. With additional effort, two or three further paints may become analysable. In contrast, none of the organic pigments were detected though it is worth checking in the future whether acrylic- or alkyd-based organic pigments are detectable, especially when access to larger d -spacings is possible. It is noted that non-invasive Raman spectroscopy is effective for organic pigments [9], for identification purposes at least, and in this respect there is good complementarity between XRD and Raman methods. Synthetic organic pigments were developed from the first half of the 20th century onwards and, consequently, it is expected that the back-reflection method is most suited to the archaeometric study of older paintings.

The efficacy of the technique for real paintings, with the complicating factors of varnish overlayers, paint mixtures and layering of paint, requires testing. The utility of current non-invasive XRD methods within cultural heritage, along with the quality of results presented in this article, provides a foundation for optimism. Systematic studies with prepared materials are planned in order to test the potential for depth analysis and to quantify the effect of varnish.

It is emphasised that high resolution back-reflection EDXRD is capable of returning very high quality crystallographic analyses entirely non-invasively. No special attention needs to be paid to the separation between the instrument and the sample other than to keep the air gap as small as possible and there is no need to consider the surface morphology of the sample. Non-invasive analyses preserve the integrity of heritage artefacts and allows more representative assessment of an object by enabling more thorough measurement sampling. Adapting analytical techniques for non-invasive application generally involves a technical compromise of some description, leading to reduced data quality. The exciting potential of the back-reflection EDXRD method within the cultural heritage field in general, and paintings in particular, lies in this lack of compromise. High quality non-invasive analysis is the holy grail of archaeometry.

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