



Technical History Articles

Colours of deception? An investigation into historic Reeves watercolours

Leonardo Pantoja Munoz^{a,*}, Aldous Eveleigh^b, Huw Jones^a^a Department of Natural Sciences, Faculty of Science and Technology, Middlesex University, The Burroughs, London NW4 4BT, UK^b School of Design, Faculty of Arts and Creative Industries, Middlesex University, The Burroughs, London NW4 4BT, UK

ARTICLE INFO

Article history:

Received 2 October 2025

Accepted 13 January 2026

Available online 4 February 2026

Keywords:

Pigment adulteration

Authentication

Spectroscopy

Mass spectrometry watercolour formulation

Historical materials

ABSTRACT

The authenticity of historical artist materials has long been a subject of interest in conservation and forensic studies yet formal investigations into counterfeit artist materials remain largely unexplored. This study investigated a set of watercolour blocks from the famous Reeves family, including samples suspected to be counterfeit due to inconsistencies in labelling. While historical records document fraudulent artist materials, no prior research has systematically analysed suspected counterfeit watercolours using advanced chemical techniques.

The aim of this research was to determine whether the dubious Reeves & Sons watercolour blocks exhibit material discrepancies indicative of counterfeit. By comparing their composition with known historical formulations, deviations in pigments, binder content, and unexpected additives were assessed.

A multi-technique analytical approach was employed incorporating physical separation, spectroscopy (FTIR, Raman and SEM-EDX), and high-resolution mass spectrometry (Orbitrap MS) to characterise organic and inorganic components. Principal Component Analysis (PCA) was used to detect patterns of formulation differences across samples.

Of the eleven pigment blocks analysed, dimensional and textual inconsistencies, unusual filler compositions and deviations in material properties, such as gum composition, provided evidence that supports the interpretation that four blocks (F1, F2, F3, and F4) are likely fakes. Historical records confirm that similar counterfeits existed, reinforcing this conclusion. Additionally, control samples spanning over 150 years exhibit consistent and expected characteristics, further highlighting the anomalies in the dubious blocks. However, the possibility of undocumented manufacturing variations cannot be entirely dismissed. The findings stress the need for further research, particularly on binder composition and broader forensic methods for identifying forgeries across other artistic media, to refine authentication processes and ensure accurate historical documentation.

© 2026 The Author(s). Published by Elsevier Masson SAS. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>)

Introduction

Material authenticity and fraud in art history

The authenticity of artists' materials plays a crucial role in art historical research, conservation decisions and the attribution of works. Beyond the replication of artworks themselves, forgery can also involve the imitation of the materials used to produce them, including pigments, binders, and commercial branding. Such practices complicate efforts to assess provenance and authenticity, particularly in historical media where industrial production and imitation often overlapped. While famous art forgers like Han van

Meegeren and Wolfgang Beltracchi [1,2] are known for fabricating entire paintings, historical evidence suggests that artist materials themselves have long been subject to adulteration and misrepresentation. From the Middle Ages through the 19th century, pigment purity was a recurring concern [3]. Cost-driven suppliers frequently extended expensive pigments with fillers or replaced them with cheaper alternatives. In other instances, manufacturers assigned misleading or proprietary names to pigments, making it difficult for artists to discern the quality or authenticity of their materials. This practice contributed to inconsistencies in historical artworks, as artists unknowingly used adulterated or mislabelled supplies.

For instance, lead white, a staple pigment prized for its opacity and handling properties, was commonly adulterated with barium sulphate (barytes or blanc fixe) to reduce costs [4]. Although

* Corresponding author.

E-mail address: l.pantojamunoz@mdx.ac.uk (L. Pantoja Munoz).

this increased the yield of the pigment, it also reduced its covering power. Similarly, the rise of synthetic aniline dyes in the late 19th century introduced concerns over the stability of colour, as many of these early industrial pigments, whether adulterated or not, proved highly fugitive. Artists such as William Holman Hunt criticised this trend, linking the unreliability of modern colours to the broader industrialisation of pigment manufacture [5].

Concerns over mislabelled or diluted artist materials led to legislative scrutiny by figures such as chemist Harvey Wiley and E.F. Ladd in the early 20th century [6].

The role of scientific material analysis in detecting forgeries

The authentication of artworks and artist materials has increasingly relied on scientific analysis. Traditional connoisseurship can be complemented, or even challenged, by techniques such as Raman spectroscopy, X-ray fluorescence (XRF), and mass spectrometry (MS), which allow experts to examine the composition of pigments, binders, and additives [7].

For instance, the identification of titanium white in a painting claiming to be from the 18th century immediately raises suspicion, as this pigment was not commercially available before the 20th century [8]. Similarly, spectral analysis can reveal whether a pigment was prepared using historical recipes or if synthetic versions were substituted [9]. Combining these scientific tools with archival research strengthens the ability to distinguish authentic artworks from altered or counterfeit pieces.

Pigments, binders, and additives: variability and substitution in historical art materials

Throughout history, the materials available to artists have been influenced by sourcing challenges, supply chain inconsistencies and intentional or unintentional substitutions. Such variations affected not only the appearance and working properties of artists' materials but also their long-term stability, leading to differences in colour, texture, and degradation behaviour among artworks. Artists traditionally relied on pigments sourced from natural minerals, plants, or insects, but the availability and quality of these materials as noted by Barnett, Miller and Pearce [10], were often subject to external factors such as geographical constraints, processing variability or trade and supply chain disruptions [10].

The composition of these materials provides valuable clues in forensic analysis. Identifying the precise formulation of a paint can indicate regional or period-specific manufacturing techniques, offering insight into an artwork's origin and authenticity.

Watercolours as a material study: the Reeves blocks and potential irregularities

William Reeves started his company in 1766. The Reeves brothers worked together from 1780 under the name Messrs Reeves. The company, which would later play a defining role in the worldwide production of commercial watercolour paint as Reeves & Sons, was founded in 1830 by William John Reeves, the son of Thomas Reeves, together with his sons James and Henry. The company revolutionised the medium in 1781 by developing the first water-soluble dry cake watercolours (blocks), making them more portable and accessible to artists [11].

Before Reeves' innovation, watercolours were traditionally prepared by grinding pigments with a gum Arabic binder to form a paste, which artists mixed with water as needed. Reeves' dry blocks eliminated this preparatory step, allowing for greater convenience.

The company underwent several name changes, reflecting its expansion and evolution in the art materials industry. Also fol-

lowing the partnership dissolution between brothers William and Thomas Reeves in December 1783, each brother established his own business, leading to parallel operations. For the complete overview see Fig. 1.

Reeves' prominence in the market also made it a target for counterfeiters, with reports indicating the circulation of fraudulent watercolour blocks falsely bearing the company's branding. As early as 1794, WM Reeves warned customers about counterfeit products, emphasizing the presence of imitation watercolour blocks that were of inferior composition. This is evident in an advertisement published in the *Derby Mercury* on April 10, 1794:

"N. B. The Nobility, Ladies, Gentlemen, and Artifts, that purchase any Colours, a c defired to take Notice, that WILLIAM REEVES is marked 'on one Side of the Cakes, and his Coat of Arms on other; for there are Counterfeits of the fame Imitation, that are of a bafe Composition. He therefore, in Juftice to the Public, by whom he is fo partially honoured, prefumes to offer the above Caution, with a Reward of FIFTY POUNDS, to any Perfon who fhall be able to difcover and convia the Party concerned in the above Forgery and Imposition."

By the late 18th and early 19th centuries, Reeves & Sons had actively incorporated warnings about counterfeits in advertisements and modified their branding to deter forgery attempts. This included variations in logos, stamps, and embossed text on their products [13].

Why watercolour materials are particularly suited for forensic material analysis

Watercolour materials are uniquely well-suited to forensic analysis due to their simple composition, and distinct physical properties. Unlike oil or acrylic paints, which contain complex binders and drying oils, watercolours consist primarily of pigments (water-insoluble), binders (e.g., gum Arabic) surfactants (e.g., ox gall), and additives / humectants (e.g., glycerol, honey, waxes or resins).

This relative simplicity allows for precise characterisation using techniques such as FTIR (Fourier Transform Infrared Spectroscopy) spectroscopy, Raman spectroscopy and mass spectrometry [9,14]. Moreover, early watercolour blocks frequently bore embossed manufacturer names or product marks, providing a durable and reliable means of tracing provenance and estimating the period of manufacture. In contrast, other contemporary pigment containers were often hand-labelled, non-standardised, or have since faded, while paint bladders, used before the invention of metal tubes, were typically unlabelled and impractical for long-term identification. Although many general manufacturing practices were described in period manuals, the precise formulations and additive proportions used by individual manufacturers were closely guarded trade secrets requiring detailed analytical verification for accurate attribution.

Analytical approach for material differentiation

The differentiation of historical watercolour materials requires a combination of physical separation, spectroscopic analysis, and statistical modelling. Fractionation techniques, such as aqueous solubilisation and centrifugation, allow pigments and binders to be separated for independent characterisation.

Spectroscopic methods, including FTIR and SEM-EDX (Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy), help identify organic and inorganic components, while mass spectrometry techniques enable the detection of trace additives. Principal Component Analysis (PCA) further aids in the recognition of formulation patterns, distinguishing between authentic materials and potential counterfeits.

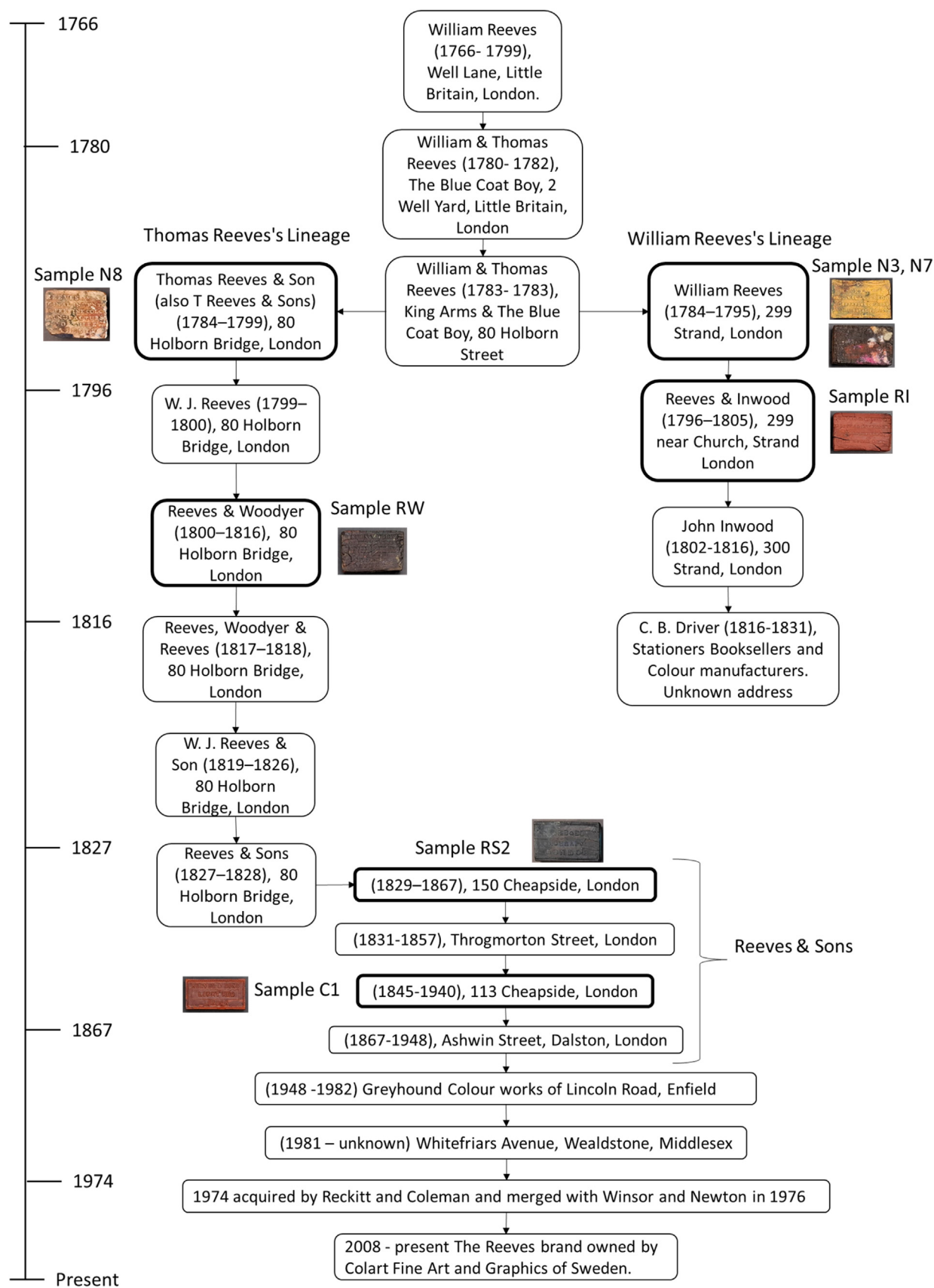


Fig. 1. Historical summary of the Reeves family company lineage, corresponding periods and main business addresses. Samples analysed in this study are illustrated and their manufacturer highlighted in bold. (Adapted from [12] and [13]) [13,12].

By integrating these methods, a comprehensive understanding of historical watercolour production, material authenticity, and the extent of fraudulent practices within the art materials market can be achieved.

The analysis of suspected counterfeit historical watercolour blocks is critical because, unlike forged artworks, fraudulent art materials often go undocumented and unstudied. There is a significant gap in research regarding the identification of fake historical pigments and paint formulations. Fake materials do not come with explicit labels identifying them as such, only forensic analysis can provide the necessary evidence. This research aims to address this gap by establishing scientific criteria for detecting inconsistencies in historical watercolour formulations.

Research aims and objectives

The aim is to determine whether the chemical and physical composition of suspected counterfeit (“dubious”) Reeves watercolour blocks (F1–F4) matches authenticated historical formulations. The Null hypothesis is that the dubious samples (F1–F4) do not differ in material composition or physical characteristics from authenticated Reeves watercolours.

To meet this aim, we compared the insoluble components (fillers and pigments), binders and additives of the dubious Reeves blocks against authenticated controls using FTIR, Raman microspectroscopy, SEM-EDX and high-resolution mass spectrometry, and quantify inter-sample differences through chemometric/statistical analyses (e.g., PCA with FDR, False Discovery Rates). We then correlated these material signatures with external indicators, misspellings, embossing/branding features and dimensions, and workability to assess whether the anomalies reflect documented historical variation or are more consistent with counterfeit production.

Materials and methods

All analysed watercolour block samples were obtained from a private collection (originally sourced from 6 different independent vendors) in the UK and permission was given to take microsamples. In the present investigation their provenance and condition were established by the physical appearance, and the embossed text. Based on their age and features, the authors have no reason to doubt that the obtained samples are representative of the historical period of interest.

Watercolour blocks were selected to cover a wide production period, with time of manufacture used as the main variable. This ensured broad temporal and material representation across known historical formulations. By including samples produced between 1780 and 1940, the study established a reference framework for normal material variation over time. This approach reduces sampling bias and allows deviations observed in the potentially dubious blocks to be interpreted as genuine anomalies rather than the result of ordinary historical changes in recipe or manufacture.

The flow chart presented in Fig. 2 shows the overall sample preparation leading to specific analysis. For the analysis, commercial gum Arabic and solvent used to carry the sample to the FTIR (acetonitrile) were used as controls.

Images of the analysed watercolour blocks (front and back) are shown in Fig. 3 and Table 1 (further discussed in section 4.3) provides a detailed description of the samples analysed in this study. The samples cover the period 1784 to 1940, representing 156 years of production by the Reeves & Sons lineage of companies. The images shown in Fig. 3 provide a visual reference for the embossed text, coat of arms, and overall condition of each sample.

Detailed images of the watercolour block samples, including close-up views with scale references for precise size measurements, are provided in the supplementary material 1. Due to the age of the blocks (approximately 240 years), some have shrunk, and the embossed text has suffered damage, making it difficult to read. To enhance legibility, Optical Coherence Tomography (OCT) was employed.

OCT imaging was performed using a Thorlabs Ganymede system with a 930 nm center-wavelength laser, a 10 kHz scan rate, and axial and lateral resolutions of 5.8 μm and 8 μm , respectively. The resulting OCT images, which provide enhanced visualization of the embossed text, are included in the supplementary material 1.

Among the samples, four are dubious (F1, F2, F3, and F4) based on distinct anomalies in their embossed text. Specifically, the samples exhibit variations in the spelling of the company name and other terms. For instance, “DM Reeves” appears on the dubious samples, whereas original blocks from the same period feature “WM Reeves,” as commonly seen in archival materials. Additionally, the word “inventer” appears on the dubious samples instead of the correct spelling, “inventor,” which is consistently found on genuine blocks. Furthermore, the use of “color” instead of the British spelling “colour” is observed in the dubious samples, whereas all other authentic samples consistently feature the latter spelling.

Interestingly, sample N7, although consistent with the general characteristics of its time, also contains the misspelling “inventer.” However, this block’s other features align with known samples from the period, suggesting that the misspelling reflects a manufacturing irregularity rather than deliberate falsification. The chemical analysis of the dubious samples was focused on F2 and F4. All microsamples were collected using a fine tungsten needle, taken from the lateral part of the blocks, approximately at their mid-height. The needle was carefully rotated and advanced into the material, effectively drilling into the block to recover both surface and subsurface particles. Further consideration of textual and graphical inconsistencies in branding/coats of arms are revisited in the discussion (section 5.1).

Molecular analysis. Raman microspectroscopy

Confocal Raman microscopy was performed using a Labram Aramis (Horiba Scientific) using a 532 nm laser (10 % power), a 50X objective, 600l/mm grating, 50 μm pinhole, 0.1–5 s integration time and average of 40 spectra accumulations, with spectra baseline corrected. The instrument was calibrated using a silicon wafer and automatic software correction (Labspec 6). All reference spectra were taken from the Soprano, Marucci et al. and Sigma Aldrich Raman databases [15,16]. All Raman spectra display intensity in arbitrary units on the y-axis. Raman spectra were baseline-corrected to remove fluorescence background prior to interpretation.

FTIR with attenuated total reflectance (ATR)

FTIR analysis was done using an Agilent Cary 630 instrument (Agilent Technologies). The instrument utilises a deuterated tryglycine sulphate (DTGS) detector and a ZnSe beam splitter, operating in the range 450–4000 and 4 cm^{-1} resolution. Sampling was carried out in ATR mode, and an average of 32 scans was collected for both background and sample spectra. All FTIR spectra showed absorbance units in the y-axis. Software used for collection was MicroLabPC.

In order to allow direct comparison and for consistency, the x-axis in all spectra shows increasing wavenumbers from left to right. FTIR spectra were analysed without normalization or baseline correction.

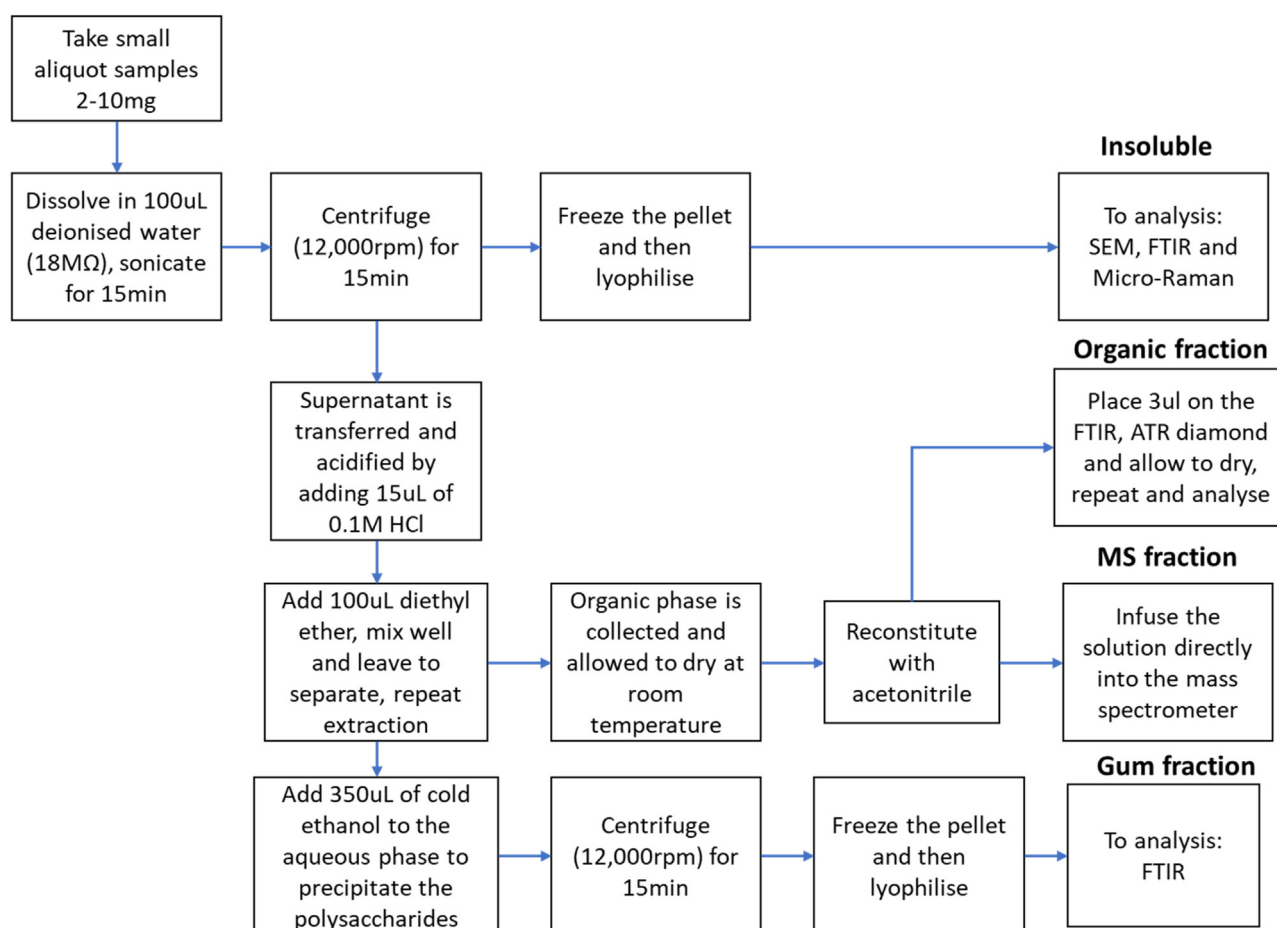


Fig. 2. Overview and details of the sample preparation performed on the watercolour samples.

Table 1

Samples used in the present study as well as their analysis using EDX-SEM, FTIR and micro-Raman spectroscopy.

ID	Description	Period	Size mm	Expected or Anomalous Text	Elemental analysis	FTIR (Insoluble)	Raman (Insoluble)
RS2	Reeves & Sons	1829–1867	31 × 18	Expected	O, Ca, C	Calcite	ND
F2	DM Reeves (Dubious 2)	1784–1795	24 × 15	Anomalous <i>DM Reeves</i> <i>Inventer Color</i>	O, Ca, Fe, N, C, Na, Al Pb, O, K, S O, Ca, S Pb, O	Prussian Blue Gypsum	Gypsum Anglesite Cinnabar
RW	Reeves and Woodyer	1800–1816	27 × 18	Expected	O, Pb, C, Br, Ca, P, Si O, Si, Br, K, C, Mg O, C, Al	Spanish Saffron	ND
N7	WM Reeves	1784–1795	28 × 19	Anomalous <i>Inventer</i>	Pb, O, K, S Pb, O	ND	Anglesite
N8	T Reeves & Sons	1784–1799	24 × 19	Expected	Pb, O, Sb Pb, Sb, O, C	Leadhillite	Leadhillite
N3	WM Reeves	1784–1795	28 × 18	Expected	O, Fe, Si, Mg, Al, C O, Mn, Fe, Mg, Ca O, Fe, Si, Ca, Al	ND	ND
C1	Reeves & Sons	1841–1940	27 × 14	Expected	O, Fe	Mica	Haematite
RI	Reeves & Inwood	1796–1805	27 × 18	Expected	O, Si	Iron oxide	Haematite
F4	DM Reeves (Dubious 4)	1784–1795	23 × 15	Anomalous <i>DM Reeves</i> <i>Inventer Color</i>	Pb, O Pb, O, C	Anglesite	Lead (II) carbonate
F1	DM Reeves (Dubious 1)	1784–1795	18 × 12	Anomalous <i>DM Reeves</i> <i>Inventer Color</i>	NA	NA	NA
F3	DM Reeves (Dubious 3)	1784–1795	23 × 14	Anomalous <i>DM Reeves</i> <i>Inventer Color</i>	NA	NA	NA

NA: Not analysed. ND: No data generated. For elemental analysis each row corresponds to a different particle with elements ordered by abundance. Calcite (CaCO_3), Prussian Blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, PB27), Gypsum (calcium sulphate, CaSO_4), Anglesite (PbSO_4), Cinnabar (HgS , PR106), Spanish Saffron (NY6), Leadhillite ($\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$), Mica (silicates), Haematite (Fe_2O_3 , PBr7), iron oxide ($\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$), lead (II) carbonate (PbCO_3 , PW1).



Fig. 3. Front and back views of the watercolour block samples analysed in this study. Labels indicate sample IDs.

SEM-EDX

Powder samples were analysed with a Phenom Pharos (Thermo Scientific) field emission gun scanning electron microscope (SEM) at high vacuum of 0.1 Pa and 15KV acceleration voltage. Samples were mounted in aluminium studs using double-sided carbon adhesive tabs (Ted Pella), no coating was performed. Elemental composition was investigated through EDX with a silicon drift detector (SDD), 60 s analysis time per sample, minimum 200,000 total counts.

Mass spectrometry

A Thermo Scientific Q Exactive instrument was used for analysis. Samples were infused directly into the electrospray source at $5 \mu\text{L min}^{-1}$ using a syringe pump. MS scans were acquired from m/z 150 to 1000 at resolution of 70,000 with AGC (Automatic Gain Control) of 3^{66} and maximum IT (Ion Injection Time) of 100 ms. The upper mass limit (m/z 1000) was selected to capture the expected range of small organic molecules, degradation products, and metal–organic complexes associated with watercolour binders and additives. After the signal stabilised data were acquired in positive and negative mode for 1 min each. The instrument was rinsed between samples by infusing $300 \mu\text{L}$ of acetonitrile at $20 \mu\text{L min}^{-1}$ (Fisher Scientific, Optima, LCMS grade 10,001,334). Data analysis was performed using Compound Discoverer v3.3. Acetonitrile used to reconstitute sample was used as blank. The list of detected ions and tentative molecular assignments is provided in supplementary material 3. In such files the “Structure” column contains the chemical structures of annotated metabolites encoded in MDL Molfile format. This text-based format describes the atomic connectivity and bonding of each compound and allows the molecular structures retrieved from the software to be stored and visualised consistently across different chemical software platforms.

Chemometrics analysis

FTIR data was analysed using Chemoface software v1.66 [17]. Files were exported to CSV format prior to analysis. A FDR analysis was performed using Python in Google Colab to evaluate the robustness of the PCA model applied to the FTIR spectral data. To generate a decoy model, the wavelengths (i.e., spectral features) of each sample were independently scrambled, thereby disrupting any meaningful correlation between wavenumber patterns and sample class. The same PCA and classification pipeline was then applied to the scrambled data. The FDR was calculated as the ratio of the decoy model's accuracy to that of the original model.

Qualitative analysis

To enrich the chemical analysis, and to provide a practical perspective we undertook a parallel qualitative study on a sub-sample of the watercolour blocks. We approached Senior Lecturer in Painting and Drawing at Middlesex University, Mr Aldous Eveleigh, a contemporary water-colour artist, for his insights into our samples. Seven blocks of watercolours were used in this part of the study (three authentic original and four of dubious provenance) coded-blindly and presented to Mr Eveleigh to work on with appropriate water colour artist's paper. He was asked for his views on the workability of the pigments, their quality of colour and texture as well as his considered opinion on their authenticity. The applied pigments on paper as well as authenticity findings are shown in Section 4.4. Additionally, the study was filmed “live” and a 32 min edited version can be viewed in supplementary material 2.

Results

FTIR and chemometric analysis

After the different fractions were separated, both the gum and organic fractions were analysed using FTIR spectroscopy (as indicated in Fig. 4). The results of these analyses are shown in Fig. 4A and B. Notably, no residue was obtained from Sample N8, which meant that no FTIR signal could be recorded for the gum fraction analysis. Consequently, the FTIR data presented in the figure relates only to the other samples, where distinct signals were observed in both the gum and organic fractions.

It was also noted in the qualitative analysis (section 4.4) that sample N8 had hardened and no pigment could be used to be applied. It can be hypothesised that over time, the block composed of basic lead carbonate (lead white) and a gum Arabic binder have undergone chemical and physical transformations that rendered both the binder and pigment effectively insoluble. The natural polysaccharide gum (most likely gum Arabic) is known to oxidise, degrade and cross-link with trace metal ions and environmental agents, reducing its water solubility [18]. In parallel, lead ions from the pigment may have coordinated with hydroxyl and carboxyl groups of the gum molecules, forming insoluble lead–organic complexes [19]. Moreover, lead white is susceptible to alteration, including carbonation (to cerussite/hydrocerussite) and other lead-salt formations such as Leadhillite, which may cement pigment particles into a dense, mechanically hard matrix [20]. The combined effect of organic binder cross-linking and inorganic mineralisation thus accounts for the inability to extract either gum or pigment upon aqueous exposure, and for the markedly increased hardness of the block.

Spectral differences among the analysed samples, as shown in Fig. 4A and B, indicate potential variations in composition. In particular, the observed shift of the polysaccharide band from 1015 to 1074 cm^{-1} may reflect oxidation and depolymerisation of the carbohydrate backbone, leading to altered C–O bonding. Alternatively, this shift could indicate coordination of metal ions, particularly Pb^{2+} , Ca^{2+} , and K^{+} , with hydroxyl or carboxyl groups of the gum polysaccharides [21,22], both processes being consistent with chemical aging. Furthermore, the presence of sharp peaks at 596 cm^{-1} and 655 cm^{-1} , most prominent in samples F2, F4 and RI are characteristic of sulphate (SO_4^{2-}) vibrational modes [23], attributable to the formation of Anglesite (PbSO_4) and Leadhillite [$\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$], as identified in supplementary material 1. It is plausible that these lead sulphate–carbonate phases became incorporated or complexed within the aged polysaccharide matrix, contributing to the material's reduced solubility and hardened texture.

In Fig. 4B, samples F2 and F4 exhibit broad absorptions at 3328 cm^{-1} , 1638 cm^{-1} , and approximately 526 cm^{-1} , indicative of strong hygroscopic behaviour. These bands correspond respectively to O–H stretching, H–O–H bending, and low-frequency Pb–O or water-libration modes, consistent with the presence of hydrated lead–organic residues. The organic material extracted into the diethyl–ether phase likely consists of free fatty acids and neutral lead–organic complexes formed through long-term degradation of the binder–pigment matrix. Early watercolour formulations occasionally included minor additions of drying oils, waxes, or natural resins, such as linseed oil, tallow, beeswax, or shellac, to enhance cohesion, gloss, or handling properties. Over time, these additives can react with lead white or other metal cations to form amphiphilic, hygroscopic metal carboxylates, which readily absorb atmospheric moisture and develop amorphous hydrated films upon drying, giving rise to the observed spectral features.

Most samples in Fig. 4B, present sharp absorptions at 2921 cm^{-1} and 2852 cm^{-1} correspond to the asymmetric and sym-

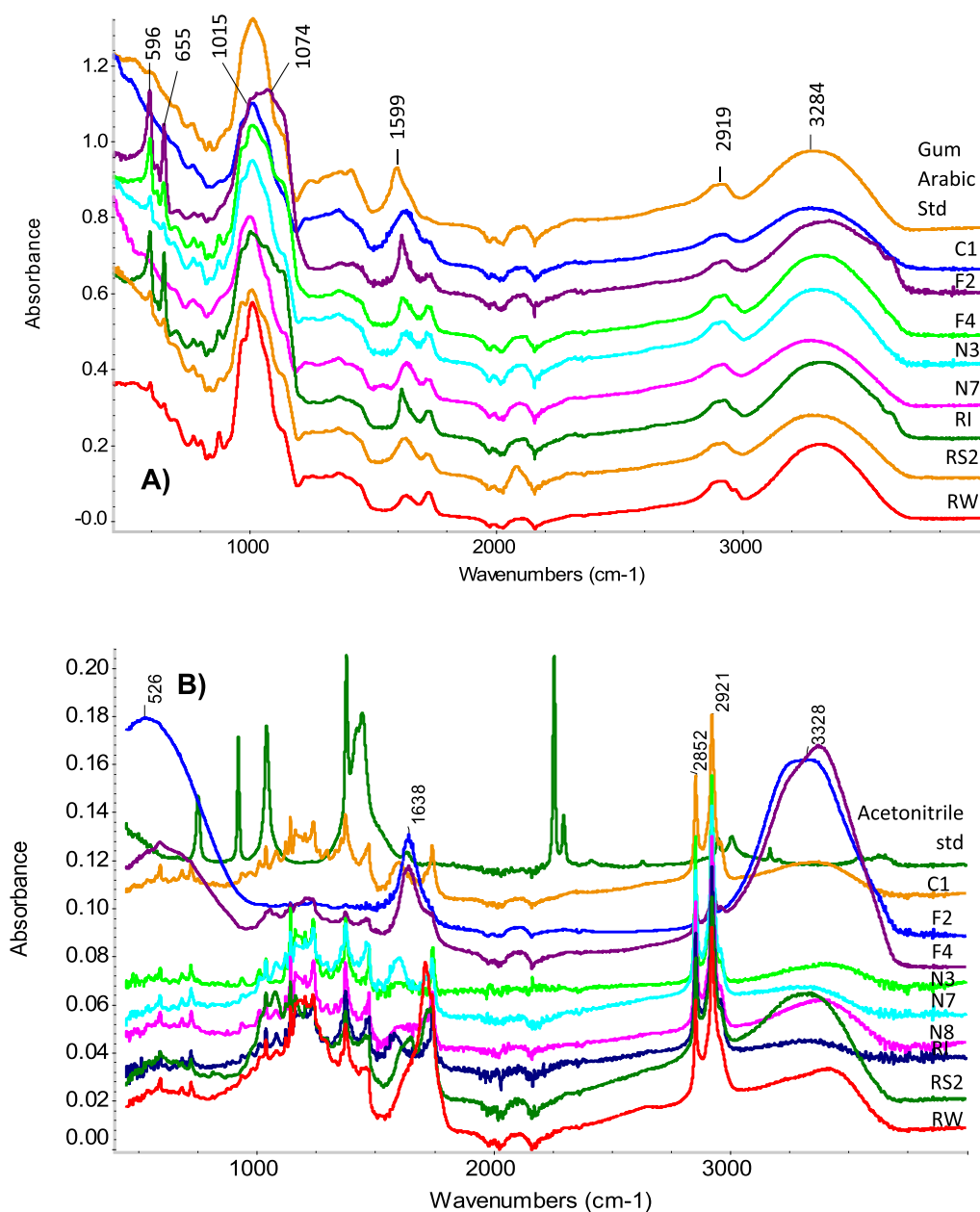


Fig. 4. FTIR analysis of separated fractions: (A) gum Arabic and (B) organic fraction.

metric stretching vibrations of aliphatic C–H bonds ($-\text{CH}_2-$ and $-\text{CH}_3$ groups). These features indicate the presence of long-chain hydrocarbons such as fatty acids, waxes, or other lipidic residues [24], which are consistent with minor organic additives historically incorporated into watercolour formulations.

It is noteworthy that sample RW in Fig. 4A exhibits a lower baseline and reduced noise compared to the other spectra. This feature likely reflects improved physical contact with the ATR crystal, rather than genuine compositional differences. Such variations in spectral intensity can sometimes be misinterpreted as chemical differences in multivariate analyses (as illustrated in Fig. 5, sample 10, RW). Although spectral normalisation can be applied to correct for baseline and intensity disparities, this process may also introduce bias by artificially amplifying minor features or altering relative band intensities. For this reason, the spectra were evaluated in their raw, non-normalised form to preserve the integrity of the comparative analysis.

In addition, Fig. 5 reveals that samples 3 and 4 (corresponding to F2 and F4) form a separate cluster, indicating a compositional distinction from the remaining specimens. The divergence of spectra 3 and 4 arises primarily from broader and less intense O–H and H–O–H absorptions ($3300\text{--}3400\text{ cm}^{-1}$ and $1650\text{--}1630\text{ cm}^{-1}$, respectively) and enhanced aliphatic C–H stretching bands ($2950\text{--}2850\text{ cm}^{-1}$). These features suggest a less hydrated, more aliphatic or lipid-enriched composition, consistent with aged or modified gum binder matrices rather than fresh polysaccharide material. This grouping indicates that these samples share similar chemical characteristics, potentially distinguishing them from the rest, which may support the hypothesis of material inconsistencies or differences in formulation. A FDR of 0.3333 was obtained for this experiment, indicating that the classification performance on the scrambled data was substantially lower than on the real data, thus supporting the presence of genuine, class-related structure in the original spectral features.

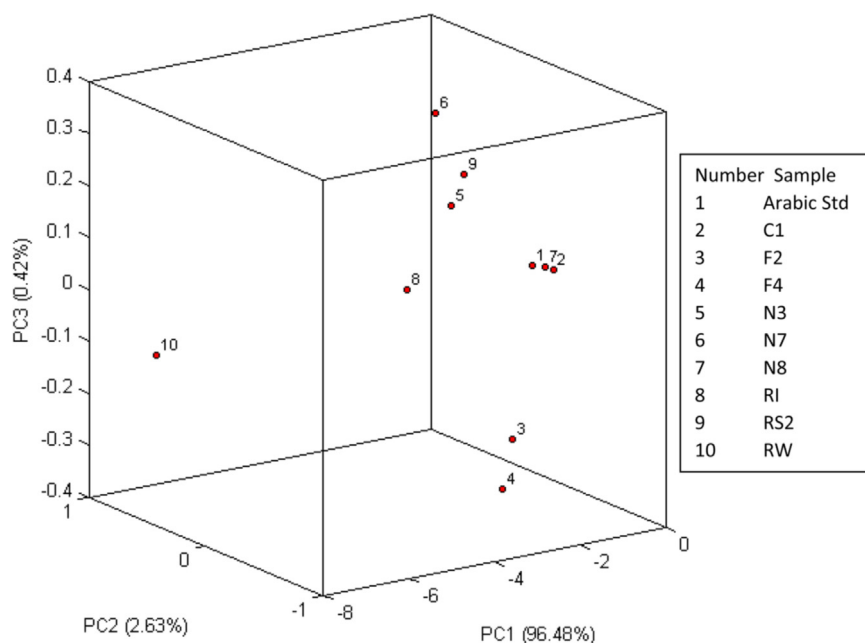


Fig. 5. Principal component analysis (PCA) of gum extracts. The first three components account for 99.52 % of the variation in the spectral features.

Similarly, the results of the multivariate analysis of the organic fraction using FTIR are presented in Fig. 6A. To further assess the relationships between samples, a cluster analysis based on Euclidean distance was conducted, as shown in Fig. 6B. The PCA results indicate that while most samples cluster closely together, samples 3 and 4 (corresponding to F2 and F4) exhibit a distinct separation from the rest. This distinction is further supported by the cluster analysis in Fig. 6B, where two well-defined clusters are observed, with F2 and F4 forming a separate group at a noticeable distance from the main cluster. The initial PCA model based on raw FTIR spectra yielded a FDR of 1.0, indicating that the classifier performed no better on real data than on scrambled data. This suggests that the PCA captured variance unrelated to chemically meaningful structure. In other words, the model was mainly describing noise, random variation, or measurement artefacts rather than meaningful patterns related to the samples' composition. Application of a second derivative transformation improved the FDR to 0.5, reflecting partial suppression of baseline and moisture-related variance, but the model still lacked robust discriminatory power.

High resolution MS analysis and chemometrics

Mass spectrometry analysis by direct infusion detected approximately 4500 unique chemical signals across all samples, PCA results are shown in Fig. 7 for both positive and negative ionisation modes. The complete list of detected ions and tentative molecular assignments is provided in supplementary material 3. These correspond mainly to fatty acids, amino acid derivatives, phenolic compounds, and minor carbohydrate fragments - chemically consistent with the degradation products of historical products used in watercolour manufacture. However, given that no statistically significant differences were observed among samples, a detailed discussion of individual compounds was considered beyond the scope of this study.

In the PCA of the mass spectrometry data (Fig. 7), Sample N8 separates distinctly in positive ionisation mode, while its corresponding signal in negative mode remains within the main cluster.

This pattern indicates that the divergence arises from preferential ionisation behaviour rather than a true compositional difference. The positive mode likely enhances the response of neutral or weakly basic species, such as residual lipidic compounds or lead-organic adducts formed during binder oxidation and mineralisation, which persist in the extractable fraction of this sample. In contrast, the absence of separation in negative mode suggests that acidic or anionic species are either absent or immobilised within the highly cross-linked, mineralised matrix. Collectively, these results imply that the distinct position of N8 in the positive-mode PCA reflects ionisation selectivity linked to its altered chemical state (as explained in section 4.1 and 4.4), rather than a substantive difference in composition.

The remaining mass spectrometry data showed no clustering, suggesting an absence of systematic compositional differences among samples. This was in contrast to FTIR analysis, which revealed distinct differences between samples F2 and F4 compared to the others. FTIR detects functional groups based on their characteristic absorption frequencies, making it well-suited for identifying qualitative differences in molecular structures. However, it may not fully capture the complexity of mixtures, particularly when component concentrations are low or absorption bands overlap [25]. Mass spectrometry, on the other hand, identifies and quantifies a wide range of molecular components by measuring their ionised forms. This allows it to provide a more comprehensive picture of the sample's composition, although its accuracy can be affected by differences in how easily molecules ionise and by interferences from other chemical species.

Because the mass spectrometry data did not show any meaningful separation between the dubious and control samples, it indicates that the composition of the ether-extractable organic fraction is largely comparable across all specimens. If different humidifiers or organic additives had been used, distinct ion profiles or clustering patterns would be expected; their absence suggests that such components are either absent or present in similar amounts, and therefore do not account for the observed differences. The differences observed in FTIR but not in mass spectrometry highlight the complementary nature of these analytical techniques.

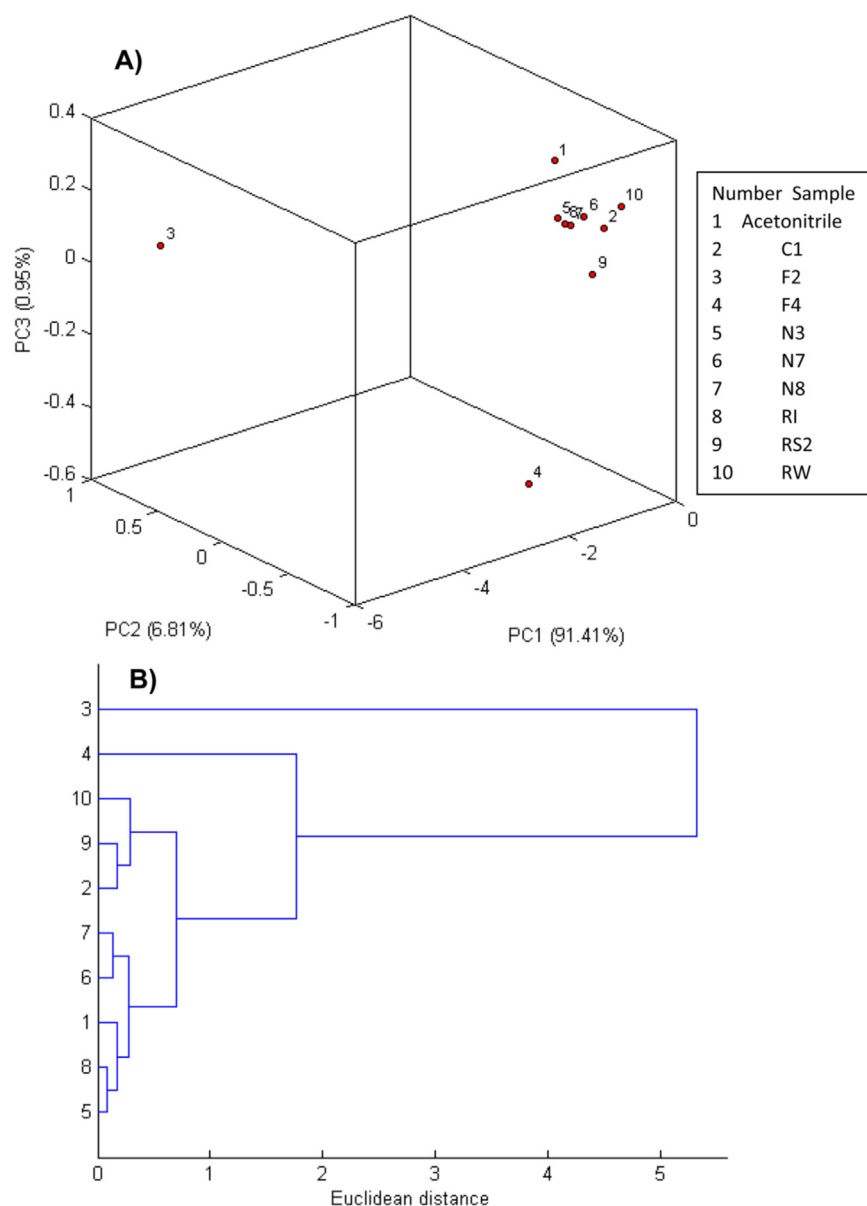


Fig. 6. A) Principal Component Analysis (PCA) of organic extracts (the first three components explain 99.16 % of the variation in the spectral features) and B) Euclidean distance, using average linkage for the first three principal components shown in A.

Insoluble residue (filler and pigment) analysis

The fractions collected after dissolution and centrifugation were analysed to determine their composition. These residues consisted primarily of pigments and non-soluble fillers. Detailed FTIR and Raman spectra are provided in supplementary material 1, while Table 1 summarises the pigments and associated inorganic phases identified across all samples. The analyses reveal that the materials comprise lead white, Gypsum, Anglesite, Leadhillite and iron oxide, all consistent with pigments and fillers historically available during the late eighteenth to early nineteenth centuries. No anachronistic or modern synthetic pigments were detected, indicating that the compositions of both authentic and dubious samples correspond to the expected historical palette and do not suggest later forgery.

The same fractions were examined by SEM-EDX, and the results are summarised in Table 1, which also includes the measured block dimensions. Dimensional analysis revealed a systematic distinction between the dubious and authentic examples, with the former

consistently smaller. This uniform size difference across all dubious samples likely reflects a distinct production format or mould size employed during manufacture rather than shrinkage caused by aging. Although minor dimensional variation can occur through binder loss or environmental factors, the consistent reduction observed here supports the interpretation of an intentional difference in original block dimensions rather than deformation over time.

Qualitative analysis

Images of the sub-sample of seven worked pigment samples on artists water colour papers together with identification of original/dubious samples is provided in Fig. 8. In addition, a full filmed account of the study is provided in supplementary material 2. The selected samples in the study displayed vastly different properties in terms of workability of application of pigment, notably sample B (N8) which was described as a “lump of rock” from which barely any pigment could be loaded onto the brush. Others, notably RS2, F3 and N7 were found to be easily workable with strong

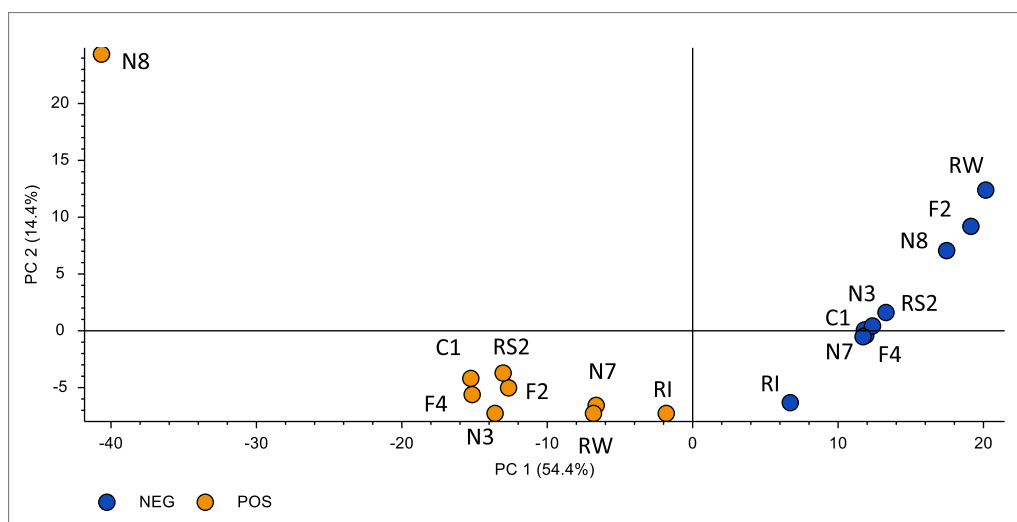


Fig. 7. Mass spectrometry principal component analysis of the organic fraction in positive and negative ionisation modes.

pigmentation and ease of application. It is notable that only two of those samples were correctly identified as authentic blocks by our study's resident artist.

Overall, however 3 from 7 of the blocks were not identified in agreement with the pre-assessment, an outcome that the authors are unsurprised by, given that pigment solubility and workability over the extended ages of these samples can lead to deterioration in gums, binding agents etc. rendering some blocks unworkable-authentic or not. This aspect of the study gave a fascinating insight into the first use of these pigments for up to 200 years and indicated that chemical analysis alone of the kind we undertook cannot predict the usability or quality of the product when used many years later.

Discussion

Textual inconsistencies in dubious samples

Historical records indicate that Reeves & Sons were aware of imitations of their products and actively warned customers about counterfeits. However, the presence of misspelled text on some authentic Reeves blocks complicates the identification of forgeries based solely on embossed markings. For instance, Jaap der Hollander (2023) documents blocks (1799) featuring "Inventer" instead of "Inventor," Fig. 9C and D, while the Whimsie Studio [26] shows the use of "colors" rather than "colours" on certain blocks (1819–1826), Fig. 9A. These inconsistencies suggest that unintentional manufacturing variations existed, making it more difficult to distinguish between genuine errors and deliberate forgeries.

To the author's knowledge, there is only one documented case of a suspected forgery; the Whimsie Studio [26] reports one block found in a box in the United States bearing the brand "Reaves" on the embossed labelling, while the coat of arms on the back is almost identical and consistent with a block from the time (1784–1790), as shown in Fig. 9B.

In the present study, the dubious samples (F1, F2, F3, and F4) display similar textual anomalies. In addition, they feature a coat of arms that, while similar to authentic Reeves blocks, notably includes a unicorn instead of the expected seated Greyhound. This suggests that the forger may have had access to an existing block or mould with a comparable emblem and saw an opportunity to fabricate the front text separately. Given the crudeness of the lettering, which appears to have been created using lead or pewter casts, and the repeated spelling mistakes, it is plausible that the

forger was either not a native English speaker or worked without careful attention to detail.

From a sociological perspective, forgery is often driven by opportunity and economic incentive without necessarily involving a high degree of historical accuracy. The motivation behind such production remains uncertain, but it is unlikely that these blocks were produced for high-value fraudulent sales in the antiques market, as the cost of replicating historical formulations would likely outweigh the potential profit in the late 19th or early 20th century. Instead, it is more plausible that these blocks were intended as substitutes for genuine Reeves products, either to be sold as lower-cost alternatives or to circumvent supply shortages. The lack of widespread documentation of similar dubious samples suggests that these were not mass-produced but rather isolated attempts to replicate a known and reputable brand.

Composition differences between authentic and dubious samples

The material composition of the dubious samples (F2, and F4) was compared against known authentic Reeves watercolour blocks to identify any inconsistencies. While elemental composition alone is not a definitive indicator of forgery, it provides valuable context when assessed alongside pigment and filler analysis.

The elemental analysis (see Table 1) did not reveal any strikingly anachronistic components, as most elements detected align with known materials used in historical watercolour production. Lead (Pb), a key component of lead white (basic lead carbonate), was present in both authentic and dubious samples, which is expected given its widespread use in historical paint formulations [27]. Similarly, calcium (Ca) and sulfur (S), associated with calcium sulphate (Gypsum) or Anglesite, were also detected across multiple samples. The absence of modern extenders or synthetic pigments is particularly notable, as the dubious blocks show signs of careless manufacture, such as poorly made embossing, where one might expect the use of non-period substitutes if they were recent forgeries. Instead, all detected components are consistent with historical materials, suggesting that the irregularities observed stem from variations in historical production rather than modern fabrication.

More revealing, however, is the presence of specific fillers and extenders. The FTIR and Raman spectroscopy analysis identified Gypsum in some of the dubious samples (supplementary material 1, FTIR sample F2). The FTIR spectra show the diagnostic sulphate absorptions at $1130\text{--}1115\text{ cm}^{-1}$ (ν_3 SO_4^{2-} asymmetric stretch)

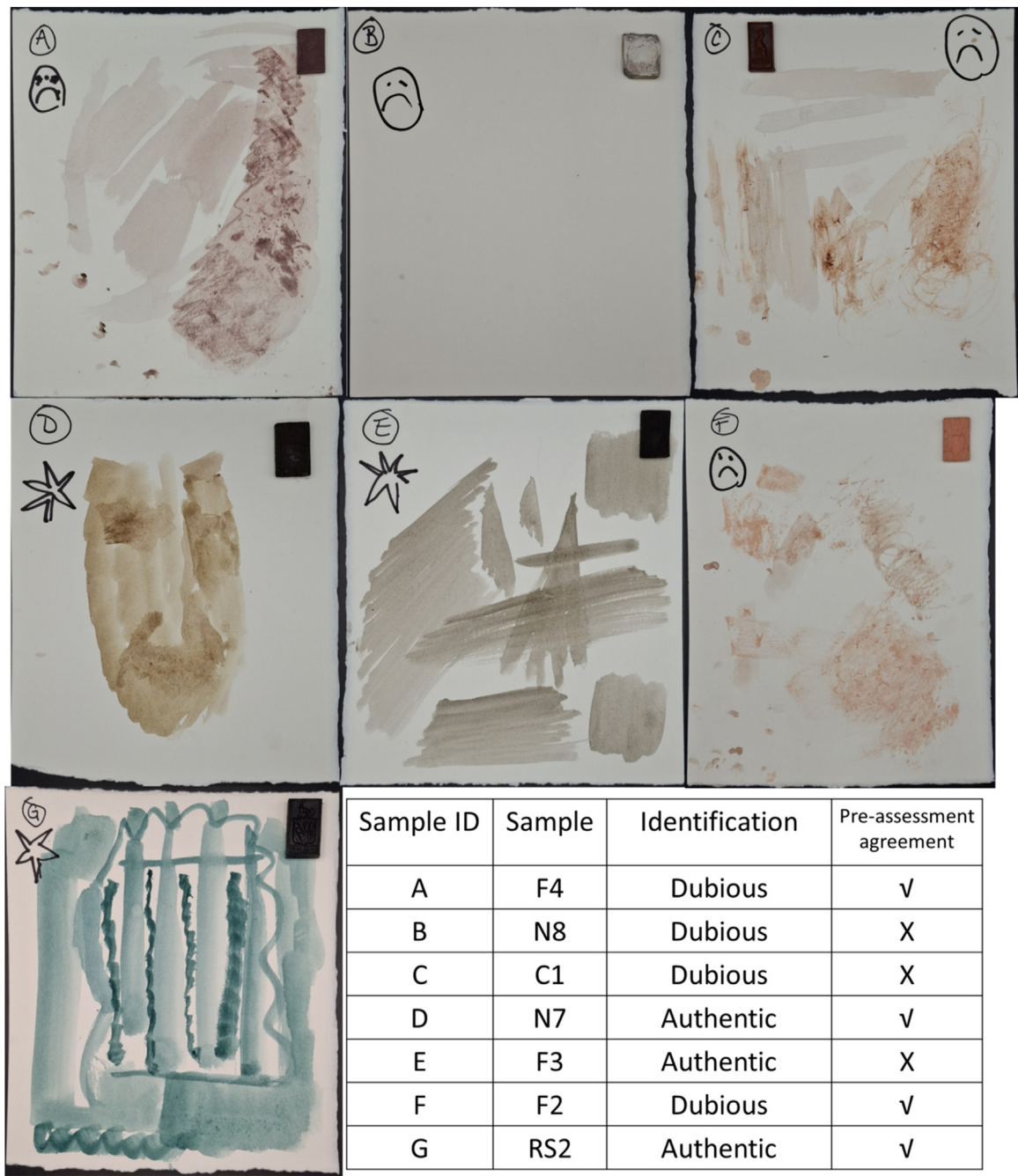


Fig. 8. Results of the qualitative analysis based on workability of application. Pre-assessment agreement refers to the initial classification of each sample as dubious or authentic prior to any analytical or qualitative testing.

and $\sim 600\text{ cm}^{-1}$ ($\nu_4\text{ SO}_4^{2-}$ bending), together with the broad $3525\text{--}3400\text{ cm}^{-1}$ O–H stretching and $1685\text{--}1620\text{ cm}^{-1}$ H–O–H bending bands associated with the structural water of Gypsum. Raman spectroscopy provides corroborating evidence, exhibiting the sharp 1008 cm^{-1} ν_1 symmetric SO_4^{2-} stretch, accompanied by lower-frequency bending modes near 415 cm^{-1} (ν_2) and $\sim 620\text{ cm}^{-1}$ (ν_4). These combined vibrational signatures align closely with reference Gypsum spectra and confirm its presence with high confidence. Although Gypsum is historically used as an extender in paints, it is not typically observed in authenticated Reeves watercolour blocks from the late eighteenth century, which generally rely on lead white and minimal inert fillers. This suggests a possible alteration in formulation, either by an unknown manufacturer or as a cost-saving measure in a non-Reeves product. Principal Component

Analysis (PCA) of the FTIR spectra (Fig. 4A; see Section 4.1) further supports this interpretation, showing that the dubious samples (F2 and F4) cluster separately from the authentic Reeves samples. This separation, driven largely by differences in the gum composition, reinforces the interpretation that these samples likely represent non-authentic or reformulated products.

Challenges in differentiating forgeries based on chemical analysis

While chemical analysis provides valuable insights into the composition of historical materials, it presents certain challenges distinguishing forgeries. One of the key difficulties arises from the variability in the materials used during different periods of manufacture as pointed in the introduction. The wide usage of



Fig. 9. Examples of Reeves watercolour blocks found in historical sources, displaying variations in the embossed text. (A) "Colors"; (B) an irregular spelling, "REAVES"; (C) and (D) "Inventor." (A) and (B) reproduced with permission from the Whimsie Studio website, credit: Ronald M. Bodoh. (C) and (D) reproduced with permission and credit: Jaap Den Hollander.

certain pigments and fillers means that even dubious samples may contain materials that are consistent with historical formulations, especially if the forgers aimed to replicate authentic production methods.

Direct infusion mass spectrometry eliminates the need for prior chromatographic separation, thereby reducing biases often introduced in untargeted metabolomic workflows. While chromatographic methods can help isolate specific compound classes and mitigate ionisation bias, the unequal ionisation efficiency of different molecules [28] introduces inherent limitations. In particular, highly polar compounds may elute rapidly and be under-represented, whereas strongly hydrophobic or resinous components, such as lanolin (wool wax), rosin (abietic and related resin acids), and mastic (triterpenoid resin), can adsorb to the stationary phase and in some cases remain irreversibly bound, reducing detection efficiency. Rosin soaps (sodium/potassium abietates), which are amphiphilic derivatives of these resins, also exhibit strong interactions with the stationary phase and may cause significant signal suppression or column contamination [29].

While FTIR and Raman spectroscopy help identify pigments and fillers, these techniques also face limitations. For instance, minor compositional variations or the use of cheaper, less common materials in forgeries may be masked by the dominant signature of more abundant components like lead white or Gypsum.

Potential alternative explanations for material discrepancies in dubious samples

While chemical and physical differences suggest the dubious samples (F1, F2, F3, F4) may not be authentic Reeves products, alternative explanations must be considered before confirming them as forgeries.

One possibility is that these samples represent early production inconsistencies. Historical records indicate that Reeves & Sons adapted different formulations and manufacturing techniques over time.

Variations in pigments, fillers, and binders could have resulted from resource availability, supplier changes, or experimentation with different compositions. Additionally, misspellings such as "Inventor" instead of "Inventor" appear in documented Reeves blocks, suggesting occasional engraving errors rather than intentional deception.

Another explanation is that these blocks were custom-made or private-label products produced by Reeves for a specific market. Companies in the late 18th and early 19th centuries sometimes manufactured bespoke materials under different branding.

Environmental factors and degradation must also be considered. Over time, exposure to humidity, air pollutants, and handling can alter materials, particularly organic components like gum binders.

If these blocks were stored under different conditions from other Reeves samples, variations in FTIR results might reflect degradation rather than fundamental differences in original composition. This was reflected upon in the qualitative study where storage and degradation factors may be more likely stronger predictors of current artists' perceptions of these pigments when used, whether authentic or not.

Without definitive archival records linking these specific samples to Reeves' documented production, these explanations remain speculative. However, they highlight the need for caution in labelling the dubious samples as outright forgeries based solely on material discrepancies.

Limitations of the current analysis and need for further studies

While the present study provides valuable insight into the composition of dubious Reeves samples, its scope is constrained by the limited number of specimens available for analysis. The small sample size restricts the ability to identify broader production patterns or confidently generalise about potential forgery practices. Given that differences were found in the gum fraction, further analysis for complete characterization of binding media, particularly the type of gum used would be useful in future studies. Recent advancements have demonstrated that partial enzymatic digestion followed by Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry (MALDI-MS) [21] can effectively identify specific plant gums, such as Acacia species, in micro-samples from artworks. Implementing this technique could provide a more detailed understanding of the materials used in both authentic and dubious samples.

Finally, the sociocultural context of counterfeiting in the art materials industry remains an underexplored area. Investigating economic incentives for forgery, the role of artist supply markets in the 18th–19th centuries, and how counterfeits were distributed and detected at the time could provide valuable context for understanding why and how these dubious samples may have been produced.

When these findings are considered alongside historical context, specifically, Reeves' documented concerns about counterfeit products and the known existence of misspelled embossed blocks, it becomes evident that the dubious samples exhibit multiple anomalies. While none of the individual material differences definitively confirm a forgery, the combination of textual inconsistencies, unusual filler composition, and documented historical counterfeit cases strengthens the argument that these samples may not be genuine Reeves products and can therefore be called fakes.

Implications for art conservation and historical documentation

The identification of forged Reeves watercolour blocks raises critical questions for art conservation and historical research. If counterfeit materials were in circulation, the assumed authenticity of artworks created with Reeves pigments must be reconsidered. Artists of the time may have unknowingly used forged supplies, meaning that genuine historical paintings could contain deceptive materials. This challenges traditional authentication methods, which often rely on the presumed legitimacy of well-known supplies.

From an art historical perspective, the existence of fraudulent art supplies forces a reassessment of how authenticity is defined. If a genuine masterpiece was created using forged materials, does this compromise its artistic or historical value? Given that artists had little control over supply chains, it would be unreasonable to discredit such works. Instead, they should be recognised as authen-

tic creations made with compromised materials, highlighting the broader issue of material forgery in artistic production.

Furthermore, the widespread reports of Reeves counterfeits suggest that these were not isolated incidents. If more forgeries existed than currently documented, pigment analysis alone may not be sufficient for dating and attribution.

In light of these findings, the study of historical artworks requires a more interdisciplinary approach. Rather than relying solely on material composition, authentication must incorporate historical context, trade networks, manufacturing inconsistencies, and distribution patterns. Addressing these challenges will enhance the accuracy of conservation efforts and provide a clearer picture of how forgery influenced artistic production in the past.

Conclusion

The combined chemical, physical, and historical evidence supports the interpretation that the examined blocks (F1–F4) exhibit material and physical divergences consistent with non-authentic manufacture. The observed inconsistencies in embossed text, dimensions, and composition, together with documented historical accounts of Reeves counterfeits, reinforce this interpretation. Control samples spanning over 150 years display the expected features of authentic Reeves watercolours, further stressing the anomalies in the dubious blocks.

Nevertheless, while the evidence strongly suggests fabrication outside of documented Reeves production, the possibility of undocumented historical variants or workshop-level experimentation cannot be entirely excluded. Continued research, particularly into binder characterisation, larger sample sets, and complementary authentication approaches, remains essential for establishing robust criteria for the identification of counterfeit or misattributed historical artists' materials.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work the author(s) used ChatGPT 5.0 in order to support language editing and academic phrasing. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the published article.

The authors gratefully acknowledge the assistance of Timur Pak, BA Film student, for capturing the video documentation of the qualitative study and for editing the final version included in the supplementary material 2. We also would like to thank Jaap den Hollander and Larry Henke, curator of the Whimsie studio for allowing us to use pictures of their work.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.culher.2026.01.011](https://doi.org/10.1016/j.culher.2026.01.011).

References

- [1] F. Kreuger, (2010). *Han van Meegeren revisited. His art & list of works*. Quantas].
- [2] G. Petri, Beltracchi: die kunst der Fälschung (Beltracchi: the art of forgery), *Law Humanit.* 18 (2) (2024) 309–312.
- [3] L. Carlyle, Authenticity and adulteration: what materials were 19th century artists really using? *Conservator* 17 (1) (1993) 56–60.
- [4] M. Stols-Witlox, The heaviest and the whitest: lead white quality in north western European documentary sources, 1400–1900, in: *The National Gallery Technical Bulletin 30th Anniversary Conference Postprints, Studying Old Master Paintings – Technology and Practice*, Archetype Publications, London, 2011, pp. 284–294.
- [5] J. Townsend, L. Carlyle, N. Khandekar, S. Woodcock, Later nineteenth century pigments: evidence for additions and substitutions, *Conservator* 19 (1) (1995) 65–78.

- [6] A. Dayan, J. Dayan, Accum and food adulteration: a forgotten bicentennial, *Toxicol. Res. Appl.* (2021) 5.
- [7] R. Goodall, Identification and authentication, in: H. Edwards, P. Vandenabeele (Eds.), *Analytical Archaeometry*, The Royal Society of Chemistry, 2012.
- [8] S. Simon, S. Röhrs, Between fakes, forgeries, and illicit artifacts—authenticity studies in a heritage science laboratory, *Arts* 7 (2:20) (2018).
- [9] M. Derrick, D. Stulik, J. Landry, *Infrared Spectroscopy in Conservation Science*, Getty Conservation Institute, 1999.
- [10] J. Barnett, S. Miller, E. Pearce, Colour and art: a brief history of pigments, *Opt. Laser Technol.* 38 (4–6) (2006) 445–453.
- [11] E.E. Barker, *Watercolor Painting in Britain, 1750–1850* October, 2004 Retrieved June 21, 2025, from http://www.metmuseum.org/toah/hd/bwtr/hd_bwtr.htm .
- [12] National Portrait Gallery British Artists' Suppliers, 1650–1950 March, 2025 Retrieved September 29, 2025, from <https://www.npg.org.uk/collections/research/programmes/directory-of-suppliers/> .
- [13] J. den Hollander, Jaap Den Hollander May, 2025 Retrieved June 21, 2025, from <https://www.jcdenhollander.nl/index.html> .
- [14] B. Sundberg, R. Pause, I. van der Werf, A. Astefanei, K. van den Berg, M. van Bommel, Analytical approaches for the characterization of early synthetic organic pigments for artists' paints, *Microchem. J.* (2021) 170.
- [15] W. Fremout, S. Saverwyns, Identification of synthetic organic pigments: the role of a comprehensive digital Raman spectral library, *J. Raman Spectrosc.* 43 (2012) 1536–1544.
- [16] G. Marucci, A. Beeby, A. Parker, C. Nicholson, Raman spectroscopic library of medieval pigments collected with five different wavelengths for investigation of illuminated manuscripts, *Anal. Methods* 10 (2018) 1219–1236.
- [17] C. Nunes, M. Freitasll, A. Pinheiro, S. Bastos, Chemoface: a novel free user-friendly interface for chemometrics, *J. Braz. Chem. Soc.* 23 (11) (2012).
- [18] C. Granzotto, J. Arslanoglu, C. Rolando, C. Tokarski, Plant gum identification in historic artworks, *Sci. Rep.* 7 (44538) (2017).
- [19] L. Masschelein-Kleiner, *Ancient Binding Media, Varnishes and Adhesives*, IC-CROM, Rome, 1995.
- [20] E. Gliozzo, C. Ionescu, Pigments—lead-based whites, reds, yellows and oranges and their alteration phases, *Archaeol. Anthropol. Sci.* 14 (17) (2022).
- [21] C. Granzotto, K. Sutherland, J. Arslanoglu, G. Ferguson, Discrimination of Aca-cia gums by MALDI-TOF MS: applications to micro-samples from works of art, *Microchem. J.* 144 (2019) 229–241.
- [22] J. Mills, R. White, *Organic Chemistry of Museum Objects*, Routledge, London, 1999.
- [23] R. Frost, T. Klopogge, Raman spectroscopy of lead sulphate-carbonate minerals – implications for hydrogen bonding, *Neues Jahrb. fur Mineral.* 12 (2003) 529–542.
- [24] A. Nuzzo, P. Buurman, V. Cozzolino, Infrared spectra of soil organic matter under a primary vegetation sequence, *Chem. Biol. Technol.* 7 (6) (2020).
- [25] P. Griffiths, J. de Haseth, *Fourier Transform Infrared Spectrometry*, John Wiley & Sons, Hoboken, 2006.
- [26] L. Henke, R. Bodoh, Reeves & Sons watercolour & Artists Supplies Catalogue c. 1830, 2013 Retrieved June 24, 2025, from <https://www.whimsie.com/index.html> .
- [27] B. Han, B. Zhang, J. Chong, Z. Sun, Y. Yang, Beauty and chemistry: the independent origins of synthetic lead white in east and west Eurasia, *Humanit. Soc. Sci. Commun.* (281) (2022) 9.
- [28] J. Fenn, M. Mann, C. Meng, S. Wong, C. Whitehouse, Electrospray ionization for mass spectrometry of large biomolecules, *Science* 246 (4926) (1989) 64–71.
- [29] N. Ghafari, S. Lekha, Challenges and recent advances in quantitative mass spectrometry-based metabolomics, *Anal. Sci. Adv.* 5 (5–6) (2024).