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Inside an Arnoldi Mushroom: Minimally Invasive Multi-Analytical Characterisation of a Nineteenth-Century Papier-Mâché Object

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Abstract

This work presents the adapted application of X-ray fluorescence (XRF) spectroscopy, Raman spectroscopy, and laser-induced breakdown spectroscopy (LIBS) for the analysis of painted historical *papier-mâché* objects, with particular focus on optimising the experimental parameters of the laser-based techniques to minimise potential damage. Mock-ups of the material, featuring different pigment finishes, were used to evaluate the analytical performance of the techniques and assess laser-induced alterations, establishing a balance between analytical signal quality and surface impact. The selected conditions were subsequently applied to a historically significant case study: a 19th-century *papier-mâché* model of the mushroom *Amanita muscaria* from the Arnoldi collection. The *papier-mâché* matrix was attributed to a mixture of a calcium-based component, including gypsum and calcium carbonate, and a silicate-based component, including quartz and kaolin. Red lead, chrome yellow, and a lithopone-based finishing layer were identified as the main pigments and surface treatments. To complement the spectroscopic analysis, ultraviolet-induced visible fluorescence (UVF) photography was used to further characterise specific pigments, while X-ray computed tomography (CT) was employed to non-destructively investigate the internal structure of the object, revealing wooden cores within the mushroom bodies and the depth of fractures. These results provide insights into the materials and conservation state of the model and demonstrate the value of combining complementary analytical techniques for the study and characterisation of fragile cultural heritage objects.

Keywords: *Papier-mâché*, LIBS, Raman spectroscopy, XRF, X-ray CT Scan, Cultural heritage

1 Introduction

1.1 Papier-Mâché: History and Previous Studies

Papier-mâché is a lightweight composite material made from paper pulp or strips bonded with an adhesive paste, enabling the production of diverse decorative and

functional objects. The term derives from the French expression meaning “chewed paper”, referring to the material’s pulped appearance [1]. Although its origins are commonly traced to ancient China shortly after the invention of paper (around 200 AD), the technique gradually spread throughout Asia and later reached Europe in the 18th century [2]. In some traditions, mac-

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erated paper was often combined with natural varnishes and fibrous materials to increase durability, allowing objects to be molded or baked into complex forms employed in decorative objects, furniture, and artistic artefacts [3].

Despite its long history and widespread use, the literature on *papier-mâché* remains largely focused on its manufacture and applications, with much information found in technical and craft literature [4]. In contrast, analytical studies of historical *papier-mâché* objects using modern scientific techniques remain relatively limited.

Among the reported studies, Manso et al. performed a micro-analytical investigation of a Portuguese *papier-mâché* sculpture, combining optical microscopy, micro-X-ray fluorescence (micro-XRF), Raman microscopy and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) to characterise the support, pigments and different polychrome layers [5]. Micro-XRF and Raman spectroscopy are particularly attractive for the study of cultural heritage objects because they enable non-destructive material characterisation (with controlled laser exposure in the latter). Micro-XRF provides elemental information but has limited sensitivity to elements with atomic numbers below that of magnesium [6]. Furthermore, the detected signal is integrated over a finite interaction volume, making it difficult to distinguish contributions from different depths. Raman spectroscopy complements this information by providing molecular identification of pigments and compounds; however, its application may be limited by fluorescence and weak Raman scattering [7]. In contrast, SEM-EDS generally requires sampling, making it unsuitable for when the preservation of the object is paramount.

More recently, Ceccarelli et al. investigated *papier-mâché* puppets using pulsed thermography and mid-wave infrared reflectography [8], demonstrating the potential of non-invasive imaging for detecting internal structures and deterioration, although with limited compositional information.

These studies highlight the need for complementary methodologies combining structural, molecular, and elemental information while minimising impact on fragile objects.

Among the emerging techniques, Laser-Induced Break-

down Spectroscopy (LIBS) has attracted increasing interest in cultural heritage applications [9, 10]. LIBS is a micro-destructive technique based on plasma formation following laser ablation of the sample surface, from which elemental information is obtained [11]. Unlike XRF, LIBS is highly sensitive to light elements, making it particularly attractive for the analysis of organic materials such as *papier-mâché*. Nevertheless, its application to cultural heritage remains limited because of its micro-destructive nature. Compared with conventional sampling techniques, however, LIBS produces substantially less damage and, when acquisition parameters are carefully optimised, the resulting surface alteration can be minimal while providing compositional information that cannot be obtained by non-destructive elemental techniques alone.

1.2 Arnoldi Collection

A representative example of a historically significant *papier-mâché* collection is the Fungi Didactic Model Collection preserved at the Natural History and Science Museum of the University of Porto. It comprises 45 life-sized models of fungal reproductive organs produced in the late 19th century and used for teaching purposes until 2015. Designed in naturalistic colours, the models supported the identification of edible, poisonous, and inedible mushroom species, reflecting the growing pedagogical interest in mycology at the time.

The models were manufactured by Heinrich Johannes Arnoldi, founder of the Gotha-based workshop Fabrik künstlicher Früchte und Pilze, internationally recognised for its botanical and mycological teaching models. Initially producing porcelain fruit replicas, Arnoldi later adopted *papier-mâché* techniques that enabled lighter, more durable, and transportable objects. His mushroom collections, commercialised from at least 1871 onwards, were distributed throughout Europe as individual models or complete educational sets. The Porto collection was likely acquired in the late 19th century through scientific suppliers associated with the former Polytechnic Academy of Porto, although no acquisition records have yet been identified.

Each model is mounted on a black quadrangular base, frequently incorporating natural moss to enhance realism, and includes labels identifying the species in Latin together with descriptive information in German. The collection is distinguished by the remark-

able detail of the fructifying bodies and developmental stages represented. Despite more than a century of classroom use and environmental exposure, the models remain largely preserved, although they now exhibit significant fragility associated with the degradation of *papier-mâché*, paint layers, and internal structural components.

The manufacturing techniques and material composition of these objects remain insufficiently understood. Contemporary descriptions indicate that the models were produced using plaster moulds filled with a *papier-mâché* and plaster mixture, subsequently assembled, coated, and hand-painted. Wooden or metallic rods were inserted internally to secure the mushrooms to their bases. However, the exact composition of the *papier-mâché* matrix, ground layers, pigments, binders, and coatings likely varied according to workshop practices and production periods. This uncertainty is significant because 19th-century *papier-mâché* production employed diverse formulations involving recycled paper fibres, vegetal gums, resins, chalk, plaster, and other additives, resulting in heterogeneous structures and conservation behaviours.

Although a previous study investigated a model from this collection corresponding to *Boletus edulis* [3], providing the first detailed material characterisation of an Arnoldi mushroom model, the manufacturing techniques and variability across the collection remain insufficiently understood.

Within this context, the *Amanita muscaria* model (fly agaric) was selected as a representative case study because of its distinctive red, yellow, and white chromatic regions. The investigation of this model contributes to a broader understanding of the material diversity of the Porto collection, Arnoldi's production techniques, and the long-term conservation challenges associated with 19th-century didactic models.

1.3 Research Aim

The aim of this study is to investigate and assess a complementary analytical approach for the characterisation of historical *papier-mâché* objects, combining XRF and Raman spectroscopy with LIBS, with particular emphasis on the optimisation of Raman and LIBS acquisition parameters to minimise potential damage.

Disposable painted mock-ups with known compositions

were used to optimise the analytical conditions and evaluate the effects of laser-based measurements, allowing the selected parameters to be applied to a historically significant object: a 19th-century *Amanita muscaria* model from the Arnoldi collection.

Complementary techniques were subsequently applied to the historical object to investigate its materials and manufacturing features. XRF, LIBS and Raman spectroscopy provided complementary elemental and molecular information, while X-ray computed tomography (X-ray CT) and ultraviolet-induced visible fluorescence (UVF) photography were employed to investigate the internal structure and support pigment identification, respectively.

2 Objects Under Study

2.1 Mock-ups

Three mock-up models were produced by the Natural History and Science Museum of the University of Porto using readily available materials to reproduce representative *papier-mâché* matrices and pigment surface conditions. As *papier-mâché* is the most fragile component of the original object, the mock-ups were used to assess its response to the analytical techniques and to optimise the analytical parameters under conservative conditions before analysing the artefact. Although the materials do not necessarily correspond to those originally used in the historical object, their known composition enabled validation of the analytical procedures and provided a suitable basis for parameter optimisation.

The *papier-mâché* matrix was prepared from Arbocel BC 200 paper pulp (cellulose fibres) bound with Tylose MH 300 P (cellulose ether) prepared as a 4 wt.% aqueous solution. A small amount of calcium carbonate was added as a filler.

Three different surface conditions were investigated. One mock-up was left unpainted. A second mock-up was painted with Van Gogh acrylic paint in the Light Oxide Red colour, corresponding to Pigment Red 101 (PR101, hematite, Fe_2O_3), with white spots produced using Schmincke Titanium White watercolour based on Pigment White 6 (PW6, titanium dioxide). The third mock-up was painted with Van Gogh acrylic paint in the Raw Sienna colour, based on Pigment Yellow 42

(PY42), a hydrated iron oxide.

The mock-ups present thicknesses between approximately 1.5 and 4.4 mm and include flat and curved surfaces representative of the original model.

2.2 Papier-Mâché Mushroom

The *Amanita muscaria* sculpture consists of two separate parts: one comprising the square wooden base, the two smaller complete mushrooms, and the stem of the tallest specimen, and the other corresponding to the detachable cap, as shown in Figure 1.

For the analytical study, the sculpture was divided into three functionally distinct regions, identified by the letters A, B, and C.

Region A comprises the square base together with the internal support visible inside the stem of the tallest specimen (A1). These components appear to be made of wood. The upper surface of the base is covered with textured friable moss elements exhibiting a brownish

colour (A2). The border of the base is painted black (A4). A paper label identifying the species is attached to one side of the base (A3), while a more detailed description is located on the bottom (A5).

Region B corresponds to the white areas, which are believed to consist of the *papier-mâché* matrix. It includes the stems (B2, B3), the gills on the underside of the cap (B4), which exhibit the characteristic undulating ridge-like morphology of this part of the mushroom, and the white spots distributed over the cap (B1).

Region C corresponds to the coloured caps of the mushrooms. These are predominantly painted red (C1) while the cap of the largest specimen gradually transitions to yellow towards the edge (C2).

Prior to the examination, the mushroom underwent conservation cleaning, which involved the removal of loose particulate matter by aspiration, followed by mechanical cleaning with a rubber block and, finally, localised cleaning using a transparent PVA-Borax hydrogel.

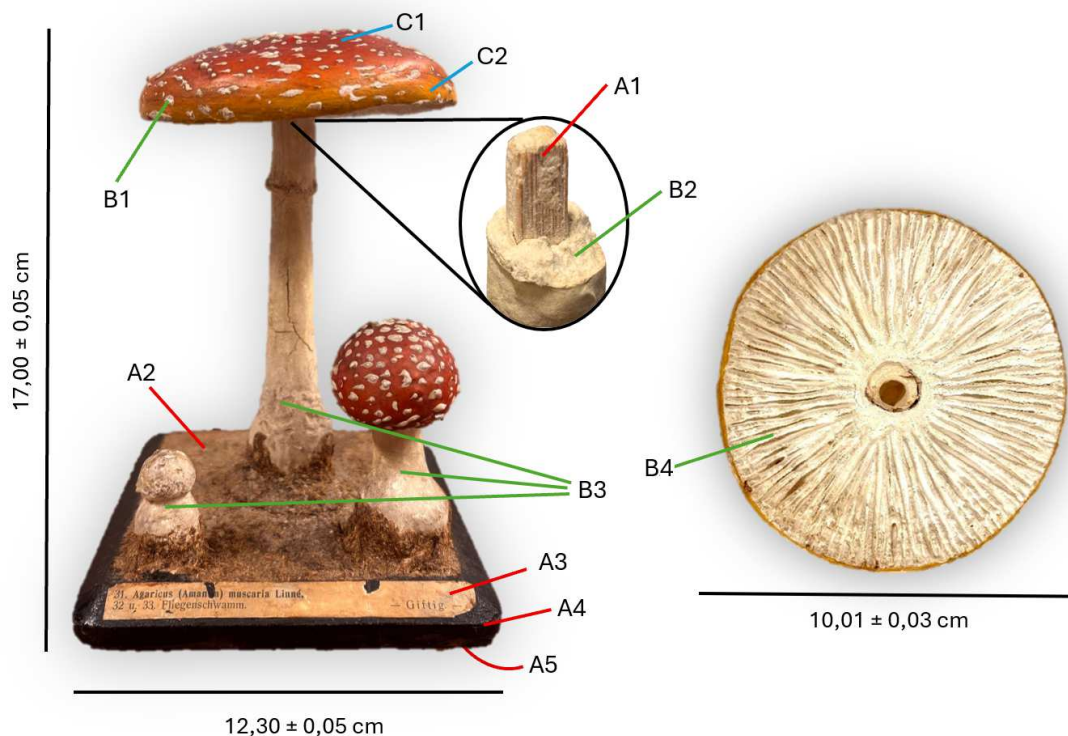


Figure 1: *Amanita muscaria* mushroom. Left: complete specimen. Right: underside of the detachable cap.

3 Methods

3.1 XRF Spectroscopy

For the measurements, the commercial Tracer 5g system (Bruker) was employed. Among the available acquisition modes, the Plants mode was chosen as the preferred option, as it best approximates the nature of the matrices under analysis. In this mode, acquisition is performed for 60 seconds at 15 keV and 60 seconds at 50 keV, with a calibrated spot size of 8 mm.

When analysing features smaller than 8 mm, the collimator was changed to the 3 mm aperture.

A boric acid reference blank was also measured during the analysis to monitor the background contribution.

3.2 LIBS

The LIBS system used in this work is based on a Q-switched Nd:YAG laser (1064 nm, 8 ns pulse duration) coupled to an 8-channel spectrometer covering the spectral range 180 – 926 nm. The optical configuration, plasma collection system, and synchronization setup have been previously described in detail [9]. In brief, the laser beam was focused onto the sample surface using a plano-convex lens ($f = 200$ mm), producing a spot size of approximately 300 μm , while plasma emission was collected through eight optical fibers connected to the spectrometer system.

All measurements were performed with acquisition parameters set to a laser repetition rate of 20 Hz, an integration time of 1.05 ms, and a gate delay of 1.3 μs .

The experimentally controlled parameter during the LIBS analyses was the laser pulse energy, adjusted by varying the Q-switch delay time. Insufficient pulse energies may not produce a plasma with enough temperature and electron density to efficiently excite the elements present in the sample, resulting in weak emission signals. Conversely, excessively high pulse energies increase the ablated volume and may lead to self-absorption, line broadening, signal variability, and unnecessary damage to the sample [11].

The tested Q-switch delay range was 300 – 380 μs , in steps of 10 μs . Since the susceptibility to laser-induced damage depends on intrinsic material properties, such as composition, structure, and the presence of binders or surface layers, the different pigments and the un-

painted *papier-mâché* matrix of the mock-ups were analysed separately.

Each experimental condition, defined by the combination of Q-switch delay and analysed material, was measured three times to evaluate the experimental variability under identical acquisition conditions. The only exception was the white paint, for which the limited available surface prevented measurements from being performed at every tested Q-switch delay.

Laser-induced damage was evaluated by optical microscopy, while the acquired spectra were evaluated using the signal-to-noise ratio (SNR), defined as

$$\text{SNR} = \frac{\text{peak height}}{\text{noise standard deviation}}. \quad (1)$$

The acquisition conditions were selected as the best compromise between maximising the SNR and preserving the integrity of the mock-up surface.

Once the optimal acquisition parameters had been established using the mock-up samples, LIBS measurements were performed on the original mushroom sculpture.

3.3 Raman Spectroscopy

The Raman imaging system used in this work has been described in detail in [12]. Briefly, it consisted of a SureLock BT-785 excitation laser diode operating at 785 nm, coupled to a Wasatch Photonics WP 785 ER spectrometer with a spectral range of 270 – 3350 cm^{-1} and a spectral resolution of approximately 8 cm^{-1} . The laser and spectrometer were fiber-coupled to a BallProbe RP 785 Raman probe (Wasatch Photonics), providing a spot size of approximately 200 μm . The probe was positioned at a working distance of about 5 cm from the sample surface.

In Raman spectroscopy, the sample is irradiated with a focused laser beam and part of the incident radiation is absorbed, producing local heating. If the delivered laser energy is excessive, the resulting temperature increase may induce irreversible changes, such as pigment degradation, carbonisation, or other thermal alterations of the sample. The total laser energy delivered to the sample is primarily controlled by two experimental parameters: the laser power and the acquisition time. For each pigment and for the unpainted *papier-mâché*

matrix of the mock-ups, acquisition times of 100, 200, 300, 400, and 500 ms were tested, while the laser power was varied in steps of 5% (where 100% corresponds to an output power of 500 mW).

Considering the SNR (also defined by Equation 1) together with the overall characteristics of the spectra, the investigated parameter space was classified into four spectral response regimes:

- **No signal:** the acquired spectrum is indistinguishable from the background noise.
- **Detectable signal:** Raman bands are distinguishable from the background noise ($\text{SNR} \geq 5$).
- **Saturation:** the detected intensity exceeds the dynamic range of the spectrometer.
- **Carbonisation:** visible laser-induced damage to the sample, confirmed by optical microscopy, and/or significant changes in the Raman bands.

Additional measurements were performed near the transition boundaries between these regimes to determine the onset of signal detection, saturation, and carbonisation more accurately. Within the detectable signal region, the optimal acquisition parameters were selected to maximise the SNR while avoiding the onset of laser-induced damage.

The selected acquisition parameters were subsequently applied to the Raman analysis of the mushroom.

3.4 Ultraviolet-induced Visible Fluorescence (UVF) Photography

The mushroom was photographed under UV illumination to visualize potential fluorescence. A UV LED source (365 nm) was used, positioned directly above the camera so that both the light source and camera were aimed at the object from the same angle. Photographs were acquired using a standard camera. This procedure was performed only on the actual mushroom specimen and not on the mock-ups.

3.5 X-ray CT Scan

Micro X-ray computed tomography (μXCT) scans were performed with the Phoenix v|tome|x L240 ($\mu/\text{n-CT}$) system (by Waygate Technologies), at the Laboratory of X-ray Micro- and Nano-Computed Tomography,

CEITEC, Brno University of Technology. Two separate acquisitions were carried out to account for the different components of the mushroom specimen: one scan of the complete structure excluding the detachable cap of the largest mushroom, and a second scan of the isolated cap.

Both scans were acquired using a 0.3 mm Cu filter to remove low-energy X-ray photons from the incident beam, thereby reducing beam-hardening artefacts and improving the quality of the reconstructed images [13]. The structure without the cap was scanned at an acceleration voltage of 150 kV and an X-ray tube current of 300 μA , with a voxel size of 60 μm . The cap was scanned at 130 kV and 300 μA , using a smaller voxel size of 32 μm to resolve finer morphological details.

4 Results and Discussion

4.1 Damage Minimization Study

4.1.1 LIBS

To evaluate the SNR, the most intense Ca emission line (Ca I, 422.72 nm), which is present in all analysed materials, was used as the reference peak. This provides a common basis for comparing the influence of laser pulse energy under different material conditions. The corresponding results are presented in Figure 2.

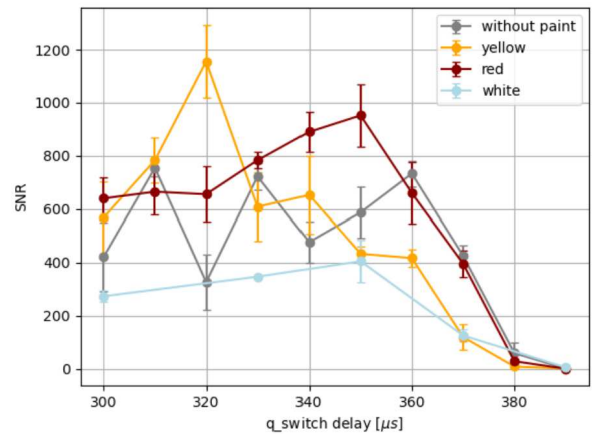


Figure 2: Signal-to-noise ratio (SNR) determined from the Ca I emission line at 422.72 nm for the matrix and each of the analysed pigments.

The SNR is shown separately for the *papier-mâché* matrix and each analysed pigment. Error bars represent the variability between measurements acquired

under identical experimental conditions. The magnitude of the error bars, together with the fluctuations observed in the overall trends, reflects several factors, including local variations in elemental concentration, transition probability, plasma temperature and electron density, self-absorption effects, laser-matter coupling, and plasma morphology [11].

In general, a marked decrease in the SNR is observed for Q-switch delays above $350\ \mu\text{s}$, indicating that the laser pulse energy becomes insufficient to generate a plasma with the same emission intensity. Of the remaining values, a Q-switch delay of $330\ \mu\text{s}$ was selected as the standard acquisition parameter because it provided consistently high SNR values across all analysed materials.

Inspection of the analysed spots revealed no visible surface alteration under any of the tested conditions for the *papier-mâché* matrix or the investigated pigments, with the exception of the red paint, which proved to be more susceptible to laser-induced damage. In this case, the surface became dull, losing its original gloss, and localised paint removal was observed, as shown in Figure 3. Consequently, the red regions of the original sculpture were analysed using a Q-switch delay of $370\ \mu\text{s}$, corresponding to the highest Q-switch delay that produced no visible paint removal.

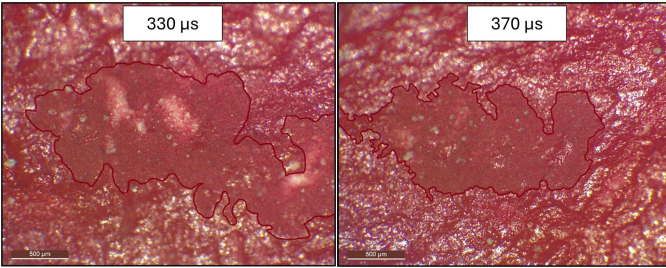


Figure 3: Microscopy images acquired at $10\times$ magnification for the red-painted mock-up. Each image shows the three shots performed at the same Q-switch delay, with the measurements positioned close to one another and forming a single damage region. The left and right panels correspond to Q-switch delays of $330\ \mu\text{s}$ and $370\ \mu\text{s}$, respectively. The damaged areas are outlined to enhance their visibility and facilitate comparison.

4.1.2 Raman

The Raman regimes identified in this study are summarised in Figure 4.

In the absence of pigment, no laser-induced degradation was observed under the experimental conditions, which is attributed to the porous structure of the *papier-mâché* matrix that promotes heat dissipation.

In the presence of pigments, a clear power threshold for degradation was observed. The red pigment was the most sensitive, requiring higher power ($\approx 7\%$) for signal detection, while exhibiting a narrow operational power window, with detectable signal obtained only below approximately 20% laser power. This behaviour is consistent with the optical properties of iron-based pigments excited at 785 nm, which may exhibit increased absorption and reduced Raman scattering efficiency, favouring local heating. Signal saturation was observed prior to visible carbonization, providing a practical indicator of proximity to the damage threshold.

The yellow and white pigments exhibited larger operational ranges, although with distinct behaviours. The yellow pigment showed an abrupt transition between signal acquisition and degradation at powers close to 30%, without a clear intermediate saturation regime.

The white pigment showed a strong dependence on acquisition time: at short integration times (100 ms), laser powers up to 70% were usable, whereas for 500 ms the power had to be reduced below $\approx 10\%$ to avoid detector saturation. This effect is attributed to detector saturation rather than sample damage, which only occurred at significantly higher power levels ($\approx 93\%$). The high reflectivity and low absorption of TiO_2 at 785 nm allow efficient Raman signal acquisition without significant heating, making the measured intensity strongly dependent on the total accumulated energy (laser power $\times$ acquisition time).

In the detectable signal region, the SNR increased with acquisition time for all pigments and the matrix. However, the values obtained at 400 ms and 500 ms were statistically similar. Therefore, 400 ms was selected as the preferred acquisition time to minimise the overall acquisition time.

Regarding the laser power, although the SNR also generally increased with increasing power, no statistically significant improvements were observed above 10% (corresponding to 50 mW). Consequently, this value was selected as the optimal operating condition, providing consistently high SNR values while ensuring safe operation across all analysed pigments.

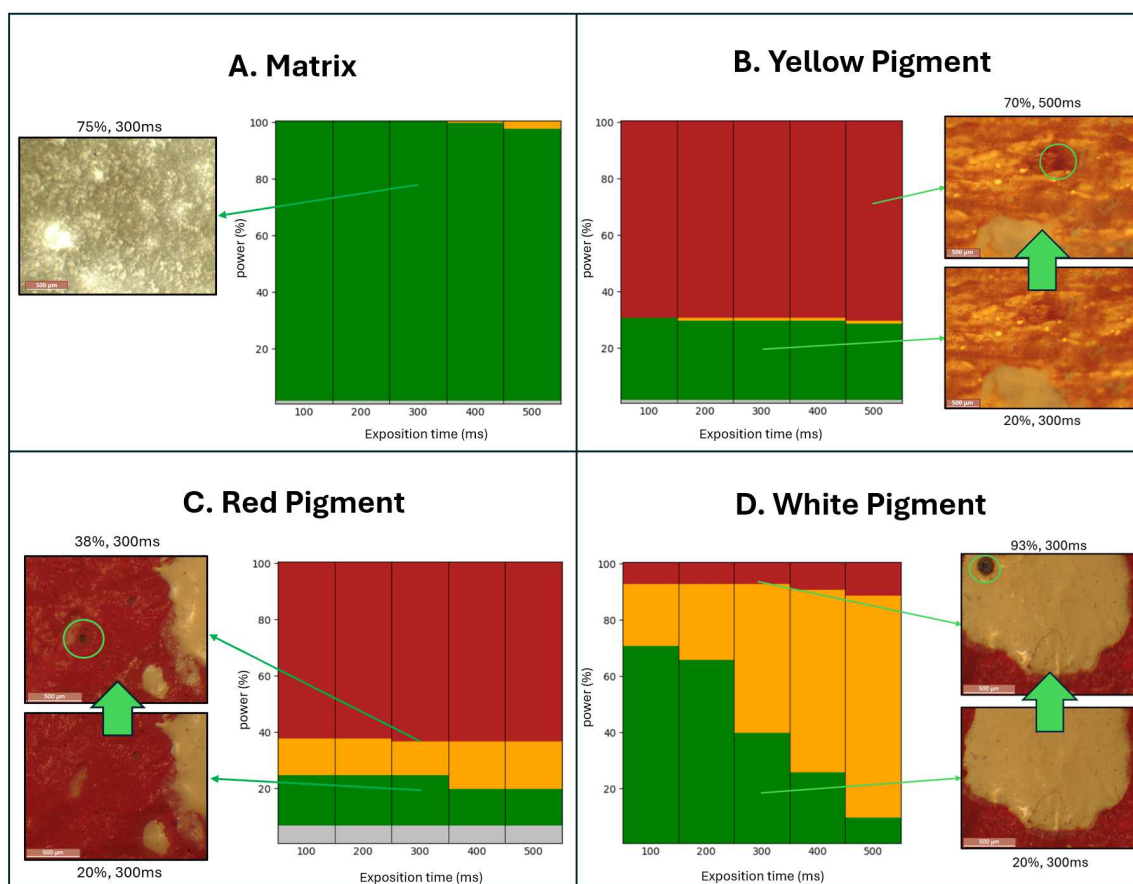


Figure 4: Raman spectral response regimes obtained by varying laser exposure time and power for the *papier-mâché* matrix (A) and the three analysed pigments (yellow (B), red (C), and white (D)). Grey indicates no detectable signal; green corresponds to a detectable Raman signal; yellow indicates detector saturation; and red indicates visible sample carbonisation.

4.2 Analytical Analysis

For material identification, the XRF, LIBS and Raman results were compared with the reference databases [14], [15] and [16].

4.2.1 Mock-up

Matrix

The elemental techniques identified Ca as the dominant element, with its characteristic emission lines presenting the highest intensities. Raman spectroscopy also revealed characteristic bands at 281, 710 and 1087 cm^{-1} , consistent with calcite (CaCO_3).

Yellow pigment

Iron was identified as the main chromophore element responsible for the pigment colour by both XRF and LIBS. In contrast, no characteristic Raman bands of

the pigment were identified, and the acquired spectrum was very similar to that of the unpainted *papier-mâché* matrix. This is most likely due to the highly diluted and translucent paint layer.

Red pigment

Iron was again identified as the main chromophore element by both XRF and LIBS. The Raman spectrum exhibited characteristic bands at approximately 290, 411 and 614 cm^{-1} , consistent with hematite (Fe_2O_3).

White pigment

Titanium was identified by both elemental techniques. The Raman spectrum showed characteristic bands at approximately 445 and 609 cm^{-1} , consistent with titanium dioxide (TiO_2).

The overall results demonstrate that the spectroscopic techniques successfully identified the declared composi-

tion of the matrix and the pigments.

4.2.2 Mushroom

XRF results were analysed first, as they provided a reliable initial assessment of the elemental composition and guided the subsequent LIBS analysis.

LIBS was then employed to complement the XRF results, confirming the elemental assignments while extending the analysis to light elements such as Li, Mg, N and O. Due to the need for precise laser focusing, measurements were more challenging on the complex geometry of the sculpture, particularly in recessed or partially inaccessible regions. With the exception of a minor, localised loss of red pigment, reported to the museum and considered readily reversible, no damage was observed on the sculpture.

Raman spectroscopy was performed afterwards to complement the elemental analyses with molecular information.

Finally, μ XCT and UVF photography were used as complementary imaging techniques.

A. Base

All the results obtained from the region identified as A in Figure 1 were characterised by the presence of Ca and K, two elements commonly found in wood as a result of mineral uptake during tree growth (see Figure 5) [17]. Al and Si were also detected and may be associated with naturally occurring inorganic mineral components of the wood, although contributions from surface contamination cannot be completely excluded, as is often the case for historical objects.

In region A2, XRF analysis revealed Ca, S, K, Si and Fe as the most abundant elements, while Mg was additionally detected by LIBS. These elemental findings are consistent with the visual observation of adhered moss fragments, indicating that natural moss was intentionally applied to the surface [18]. In the same region, particularly around the mushroom stems, dark blue fluorescence was observed under UV illumination (Figure 8). This fluorescence is most likely associated with the adhesive used to attach the moss to the wooden base.

XRF revealed a marked increase in Fe intensity at spot A4. This may be associated with the black paint ap-

plied to the border of the wooden base, suggesting the use of an iron-based black pigment, such as magnetite (Fe_3O_4) [19].

The A3 and A5 spots, located on the paper labels, exhibited the highest S intensities within the wooden base. This element may be associated with the manufacture or treatment of the paper, such as sizing agents or other additives, although contributions from the printing inks cannot be excluded.

No identifiable Raman signal was observed, with the spectra showing a broad fluorescence background.

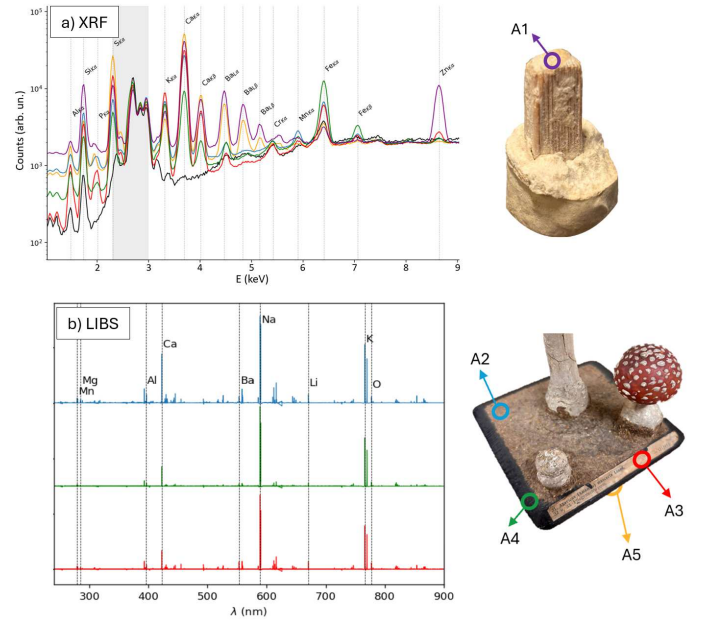


Figure 5: XRF and LIBS results of the base of the mushroom model.

B. Matrix

The analysis of the white regions revealed a slight compositional difference between a superficial layer (approximately 0.3 mm thick), corresponding to measurements at spots B3 and B4, and a more massive internal component, accessed through B2 (Figure 6). This distinction was supported by the μ XCT observations (Figure 9), where a lighter layer can be observed at the surface of the stems. In addition, μ XCT analysis revealed the presence of internal wooden supports not only in the largest mushroom, where the structure is visibly exposed, but also within the smaller specimens. As a consequence, the penetration depth of X-rays may allow contributions from these internal wooden struc-

tures in certain measurements, particularly in regions where the effective path length through the material is reduced.

Measurements acquired in B3 and B4 showed elevated levels of Zn, Ba and S, with their intensities increasing proportionally. This correlation strongly suggests the presence of barite (BaSO_4) and zinc-based compounds, such as ZnO or ZnS, materials that, when combined, may form lithopone-type pigments. Characteristic Raman bands were identified at approximately 461 and 985 cm^{-1} , consistent with BaSO_4 (barite), confirming the presence of this compound (see Figure 7). This superficial layer exhibited turquoise fluorescence under UV illumination, irregularly distributed across the stems and gills. Such behaviour is consistent with the presence of zinc-containing compounds and supports the interpretation of this layer as a surface finishing.

In contrast, measurements obtained from B2 showed a relative decrease in Ba, Zn and S intensities, although these elements remained present at significant levels, suggesting their use as distributed fillers within the *papier-mâché* matrix. In these internal areas, increased counts were observed for Ca, Si and Al. The elevated Ca signal indicates the likely presence of a calcium-based phase, possibly gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or calcium carbonate (CaCO_3). The detection of Si suggests the presence of quartz (SiO_2), commonly used as a mineral filler. The simultaneous presence of Si and Al may also indicate the presence of kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$).

The greatest uncertainty remains in the white spots (B1), which exhibit an elemental composition broadly similar to that of the mushroom stems and gills (B3), but with different relative proportions. The elements characteristic of the superficial material in B3, particularly Ba and Zn, are still detected in B1, although at lower intensities. Conversely, Ca is more intense than in B3, approaching the levels observed in B2, although it does not reach the same intensity. This intermediate composition suggests that the white spots may correspond to a mixture of the superficial material and the underlying bulk matrix. This is consistent with their apparent three-dimensional relief, as the lithopone-containing component would provide the white coloration, while the calcium-rich matrix may have contributed to their volume and structure.

The μCT observations show that the white spots ex-

hibit attenuation similar to that of the superficial layer of the matrix (Figure 9). In addition, the fluorescence observed under UV illumination was consistent, although non-uniform (see Figure 8), suggesting the presence of ZnO. The observed variations in fluorescence are more likely attributable to effects associated with ageing or degradation than to differences in the composition of the white spots; however, this interpretation cannot be confirmed based on the available observations.

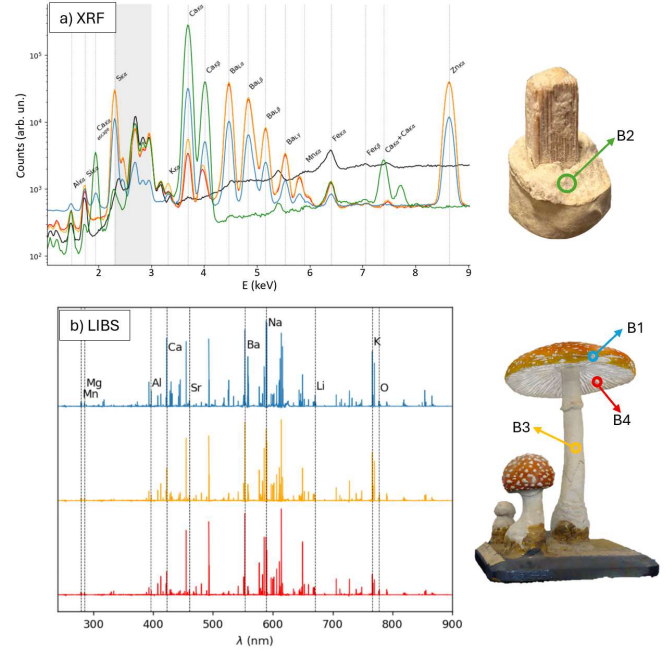


Figure 6: XRF and LIBS results of the matrix of the mushroom model.

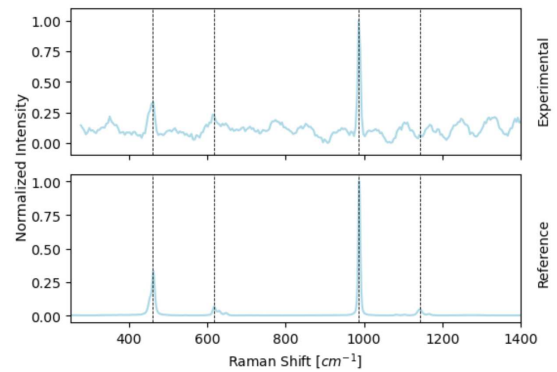


Figure 7: Raman spectra of the taller stem B3 (upper panel) and barite reference spectrum from the RRUFF database (lower panel) [16].

Beyond providing information on the internal construction of the sculpture, the μ XCT results allowed the depth and extent of the observed fractures to be assessed. Such information can support future conservation and restoration decisions by identifying vulnerable regions [20, 21].

In the removable cap, a fracture already visible to the naked eye was found to extend continuously along approximately half of its perimeter. The μ XCT data confirm that this fracture traverses the entire thickness of the *papier-mâché* layer, propagating through the full extent of the material. Its progression is limited only by the geometry of the object, terminating where the internal region becomes hollow and no further structural material is present.

At the junction between the removable cap and the wooden stem, a denser material with a cardboard-like appearance was also observed. This layer appears partially detached from the surrounding *papier-mâché*, with visible gaps at the interface as well as internal discontinuities and fractures within the material itself.

The fracture identified in the larger mushroom stem occurs in a region where the *papier-mâché* layer surrounding the internal wooden support exhibits a non-uniform thickness distribution. The wooden core itself shows a slight curvature, and is therefore not perfectly aligned with the external geometry. This geometric mismatch leads to a mechanically weak region. In this area, a crack is observed that propagates circumferentially around the structure, indicating a failure of the outer layer along the entire perimeter.

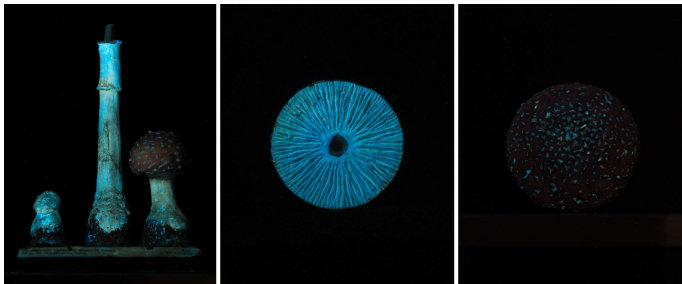


Figure 8: UVF Photography.

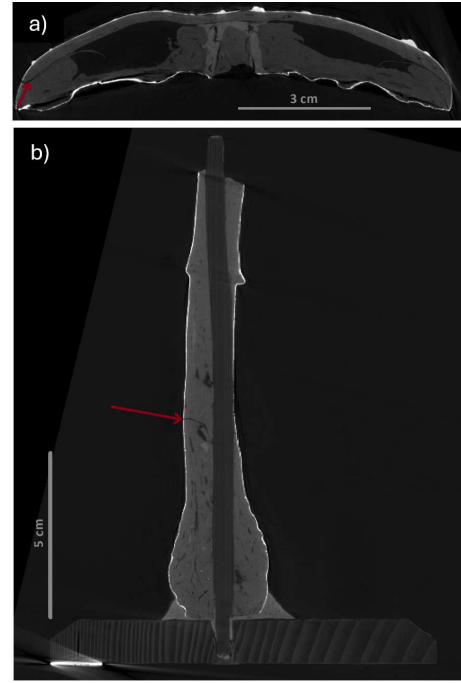


Figure 9: μ XCT Scan of the (a) cap and (b) base with the two small mushrooms and tall stems. Fractures indicated by red arrows.

C. Pigments

In this case, both XRF and LIBS provided reliable elemental information to infer the possible pigments present, whereas no signal was detected in Raman spectroscopy. One possible explanation is that the pigments present may be amorphous or poorly crystalline, which significantly limits Raman detectability. Additional contributing factors may include fluorescence interference, low pigment concentration, or masking effects caused by overlying varnish or surface coatings.

No sharply defined boundary was observed between the red (C1) and yellow (C2) regions; instead, a gradual transition from dark red at the centre to yellow near the edge is evident. Along this transition, a progressive increase in Pb intensity was observed in XRF, together with the gradual appearance of Cr in the yellowish regions (Figure 10). LIBS results further confirmed the presence of Cr exclusively in the yellow regions. These results suggest that the red pigment may be associated with Pb_3O_4 (red lead), while the yellow pigment may correspond to PbCrO_4 (chrome yellow).

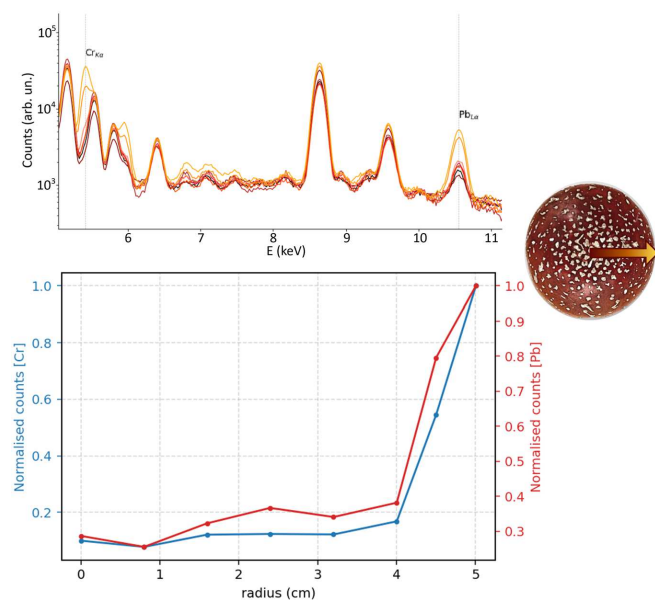


Figure 10: XRF results of the red and yellow pigment regions across the mushroom cap, showing measurements taken from multiple spots along a radial transect from the centre (red region) towards the outer edge (yellow region).

5 Conclusion

This work demonstrates a minimally invasive analytical approach for the investigation of fragile historical *papier-mâché* objects, combining elemental, molecular and structural information while explicitly assessing the risk associated with laser-based techniques. It also represents a step forward in the characterisation and cataloguing of the Arnoldi collection. The fragility of the *papier-mâché*, diverse pigments, and internal structures make these objects particularly suitable for adaptive and minimally destructive analytical approaches.

XRF, LIBS, and Raman spectroscopy were used for chemical characterisation. XRF provided non-invasive elemental information, while LIBS complemented it through its sensitivity to light elements and predominantly superficial analysis. To the best of our knowledge, this is the first reported application of LIBS to a historical *papier-mâché* object, with minimal red paint removal as the only damage observed throughout the analysis. Raman spectroscopy provided direct molecular information, enabling pigment and compound identification in mock-ups and selected sculpture regions, although weak signals and strong fluorescence limited

its application.

Most of the mushroom’s components were successfully identified. The wooden base contained elements characteristic of natural moss, while the iron-rich black pigment on the border may correspond to magnetite. The *papier-mâché* matrix was rich in Ca, consistent with calcium carbonate fillers and possibly gypsum, while Si suggested quartz. A denser superficial layer rich in Ba, S, and Zn was also detected, with heterogeneous UV fluorescence suggesting a degraded lithopone-based finishing layer. The white spots had a composition similar to the *papier-mâché*, while the red and yellow pigments were identified as red lead and chrome yellow, respectively.

Complementary X-ray CT revealed an internal wooden structure in the three mushrooms, as well as fractures in the cap and larger stem. These observations revealed the internal extent of the damage and localised thinning of the paper paste.

The study characterised the conservation state, internal structure, and constituent materials of the object. The methodology shows potential for application to other collection objects and similarly fragile cultural heritage materials, highlighting the importance of adapting analytical parameters and combining complementary techniques.

Author Contributions

LRP performed all experimental measurements, analysed and interpreted the spectroscopic, photographic, and CT data, and wrote the manuscript. DC and RC contributed to the XRF and LIBS measurements and provided training and guidance on the application of these techniques. EZ, JK, and TZ facilitated access to the CT facilities and provided the infrastructure and laboratory environment required for the CT measurements. AF and CR provided the historical object, contributed to the interpretation of the analytical results based on their expertise in conservation, historical materials, manufacturing processes, and the history of the object, and wrote the section of the manuscript concerning the history of the collection to which the object belongs. PAJ and NAS supervised the research and contributed to the interpretation and discussion of the results. DG supervised and coordinated the research, defined the project tasks, provided scientific

guidance, and contributed substantially to the writing and formulation of the manuscript. All authors reviewed and approved the final manuscript.

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Data Availability

The authors confirm that the data supporting the findings of this study are available within the article. Additional raw spectral data are available from the corresponding author upon reasonable request.

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