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Review

A Closer Look at Heritage Systems from Medieval Colors to Modern and Contemporary Artworks

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Abstract: This microreview, conducted by interdisciplinary teams, examines complex heritage material systems, such as medieval colors and modern and contemporary artworks. Our multi-analytical approach, a significant aspect of our research, is a means to this end. The conservation of works of art is our shared goal, as it ensures their accessibility and the transfer of cultural heritage to future generations. We seek to interpret the damage, usefulness, and innovation of the experimental design in this context. As Jan Wouters rightly points out, "The terminology used nowadays to describe the potential damage to objects caused by analysis should be refined beyond the destructiveness/non-invasiveness polarization. A terminology should include at least degree level intervention (low, medium, high), usefulness, and innovation". Complementing micro- or sub-micro-sampling with the appropriate analytical methods is crucial, as exemplified in medieval, modern, and contemporary collections studies. Finally, a novel perspective for exploring the information contained in the multiscale heterogeneity of organic historical materials is envisaged, and it includes UV/Visible photoluminescence spectral imaging using a low-intensity ultraviolet synchrotron beam.

Keywords: medieval manuscripts; plastic heritage; multi-analytical approach

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1. Introduction

1.1. From Medieval Colors to Modern and Contemporary Artworks: How to Study and Preserve

The conservation of works of art makes them accessible and will ensure the transfer of cultural heritage to future generations [1–5]. Thus, understanding the materials that make up works of art is crucial, as very few are simple. Indeed, it is not uncommon to find a heterogeneous mixture of organic and inorganic materials, whether animal or vegetal pigments, dyes, binders, polymers, minerals, semiconductors, alloys, or metals, when examining a work of art. This makes these objects complex heritage systems. Contemporary Art and the range of plastics and additives used over the last century pose formidable challenges to conservators and scientists due to the intrinsic susceptibility of materials to degradation, much of which needs to be better understood. Whether they are ancient or modern materials and how they have been manipulated, synthesized, and employed all contribute to this unique physical record of our past. Indeed, the complexity of constituent materials makes the study of art a fascinating challenge, and various approaches have been developed to examine our cultural heritage [1,5,6]. This microreview looks at complex

heritage material systems, such as medieval colors and modern and contemporary artworks. This research is carried out by the authors, within interdisciplinary teams and using a multi-analytical approach [5,7].

1.2. Interpreting Damage, Usefulness, and Innovation

In the realm of cultural heritage studies, the terms "destructive analysis" and "non-destructive analysis" or "non-invasive" are expected to be found. We have also often employed this terminology [8]. However, it is possible that these terms do not accurately represent reality, as was pointed out by Jan Wouters in Pure and Applied Chemistry [9]. Given that most techniques are based upon the interaction of radiation with matter, there will always be consequences for the artwork, which may occur at the molecular level and, as such, can be small or invisible to the naked eye [10]. So, it is essential to remember that some of these so-called "non-invasive" techniques, which are increasingly used in the cultural heritage field, like Raman microscopy and X-ray fluorescence (XRF), use intense and high-energy radiation [11–13]. In the case of Raman microscopy, a specialized operator will take special care to guard against these damages. Regarding XRF and XRD mapping of manuscripts and paintings, which may range from 24 to 60 h, systematic studies are required to ensure it is safe and will not impact the artwork in the next 10 or 20 years.

As stated by Wouters, "The key feature in this discussion is the way one interprets damage". In fact, "Sometimes, techniques applied directly to the object are called non-invasive. Although the term is correct since it is a non-sampling technique, the qualification may be misleading in terms of destructiveness (...)". It is better to distinguish these analytical techniques in situ, without the need for micro-sampling or requiring micro-samples; in this latter case, it will be helpful to describe the size and, if possible, the weight of the micro-sample.

The basis for the experimental design is the degree of usefulness and innovation that will allow the assessment of the object's conservation condition or the discussion of a conservation treatment—within an interdisciplinary approach that allows for obtaining the most relevant information, causing the least damage possible. In other words, for each case, we need to reflect upon the damage versus benefits ratio. As very wisely described by Jan Wouters [9],

"The terminology used nowadays to describe the potential damage to objects caused by analysis should be refined beyond the destructiveness/non-invasiveness polarization. A terminology should include at least degree level intervention (low, medium, high), usefulness, and innovation".

1.3. Micro-Sampling Techniques as a Key Advantage

One of the pivotal aspects of the study of cultural heritage, whether through the analysis of micro-samples or the use of micro-analytical techniques (either in situ or on the samples), is the relationship between a very small sample and the larger work of art, which is inherently heterogeneous—and mainly if the sample is representative. To surmount this challenge, using in situ imaging techniques and in situ examination using suitable microscopy is fundamental before any sampling. Samples of works of art are unique, and techniques continually evolve to study materials. It is likely that, with advances in analytical science, we will be better equipped to address the questions that will allow the preservation of our cultural heritage [1].

It is not always possible to answer some of the critical questions posed by conservators specifically for conservation without careful sampling and suitable study with reasonable analytical techniques, even when instrumentation and methods can travel to an object. Internationally, conservation scientists strive to answer conservation-driven questions, where the integrity of an object should be the ultimate aim. Sampling may be necessary when instrumentation cannot travel or questions need to be sufficiently motivated. Thus, micro-sampling techniques pose a crucial advantage and are increasingly used in studies—these invisible or minute samples can yield fundamental knowledge for conservation.

Much of the knowledge of the materials of our past has been gained through microscopy and micro-analytical techniques [1].

2. Medieval Colors in Illuminated Manuscripts: How to Study and Preserve

2.1. How to Preserve Medieval Manuscript Illuminations

In 1998, the challenge—from the curators and conservators at the Portuguese National Archives—was "what can science do to restore and preserve medieval manuscript illuminations?" To address this challenge, we started with the first project in 2000 to tackle the color of manuscript illuminations and their preservation. An interdisciplinary team was assembled, and the best modus operandi was tested with Art Historian Adelaide Miranda. The team members are described in Section SM1. The team proved ideal and established the roots for a life-term commitment to studying medieval illuminations. Merging art history, molecular sciences, and codicology has been instrumental in this work, with three funded projects by the Foundation for Science and Technology (FCT) [14]. This research started on the monastic production of the monasteries of Lorvão, Santa Cruz, and Alcobaça during the 12th and first quarter of the 13th centuries (the Romanesque period) [14,15]. Other manuscripts were studied, which included the Ajuda Songbook (end of the 13th or beginning of the 14th century), books of hours (late 14th and 15th centuries), a winter breviary (the 14th century), and the first page of a Portuguese Renaissance Charter (1512), see Figure 1. For more details on this research, please see our latest microreview [16].

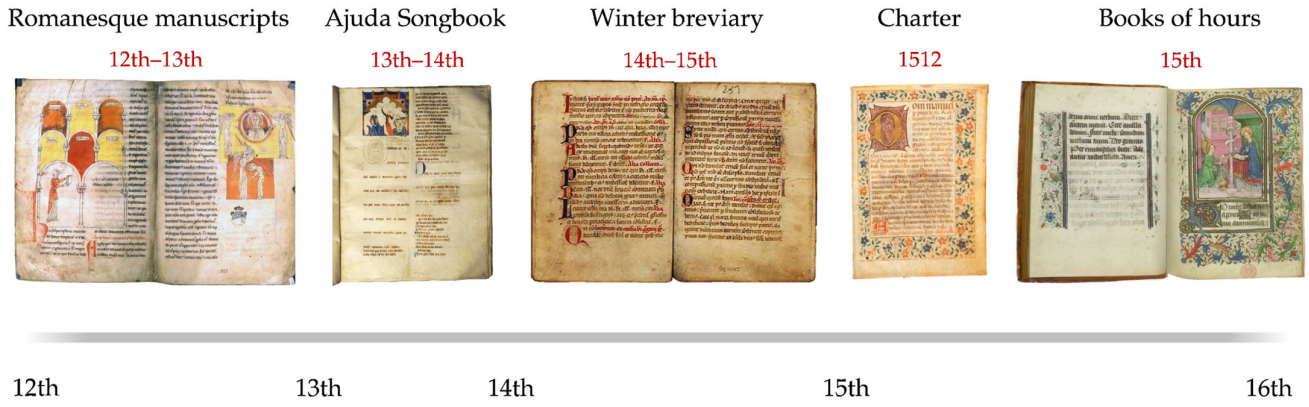

Figure 1. Timeline of the manuscripts studied by our team.

So, we would like to emphasize how misleading it can be to pit "testing that requires a micro-sample" against "in situ testing", exemplifying this within the context of the study of illuminated manuscripts. In our modus operandi, the area selection is based upon and supplemented by in situ techniques [5]. Micro-samples taken under a microscope are invisible to the naked eye and weigh less than 0.1 micrograms, possibly nanograms (it was not yet possible to obtain their weight, even though microscales have been used, which measure weights in micrograms). As a result, micro-sampling minimizes manuscript handling, and in situ techniques reduce the number of micro-samples collected, obtaining quality information and a complete paint description. Given the fragility of the manuscripts and the illuminations, to obtain a molecular characterization, we concluded that it would be less damaging to study in depth a selected set of micro-samples that represent the observed colors and degradations than to use the various necessary techniques in situ, which would a require much larger time of analysis of the manuscript. Thus, in our first project, we concluded that informed micro-sampling was essential for understanding the degradation patterns underway and the full complexity of these colors [5,14].

If safely kept, these precious samples are relevant and crucial, and time is necessary to deal with their complexity. Understanding these complex colors is a dynamic process that thrives on continuous study and innovation. Our knowledge about colors constantly expands, reflecting the evolving nature of science. Our commitment started in 2000, so

we have approached this fascinating topic for over twenty years. In the end, following Pasteur's belief in "not being able to conserve what we do not know well" ("il n'est pas possible de bien conserver ce que l'on connait mal"), it becomes urgent to advance knowledge regarding the original materials that make our cultural heritage, ensuring its conservation and transfer to future generations [17].

2.2. *Advanced Methods of Analysis for the Study of Medieval Manuscripts and Their Colors*

Our group has consistently studied medieval color formulations in illuminated manuscripts; see Figure 2 [5,18–22]. Considering that we are studying a book instead of single pages, the best choice is to use analytical techniques that do not require mapping. XRD and XRF mapping of these manuscripts may imply more than 24 h per page, and we have yet to determine the impact of these high-intensity radiations on the tempera and colorants that make up these precious colors [1,13]. Moreover, subjecting the manuscript to an extended analysis time forces the bookbinding to open, compromising its integrity. Advanced methods of analysis are thus used to identify all the components present in medieval paint (the paint formulation), including colorants, binders, varnishes, and other additives, as exemplified below. These components are essential for medieval paint's applicability and durability. Our modus operandi was created during our first project, and since then, our understanding of these complex systems has brought enormous innovation [5]. We will briefly describe our modus operandi [5].

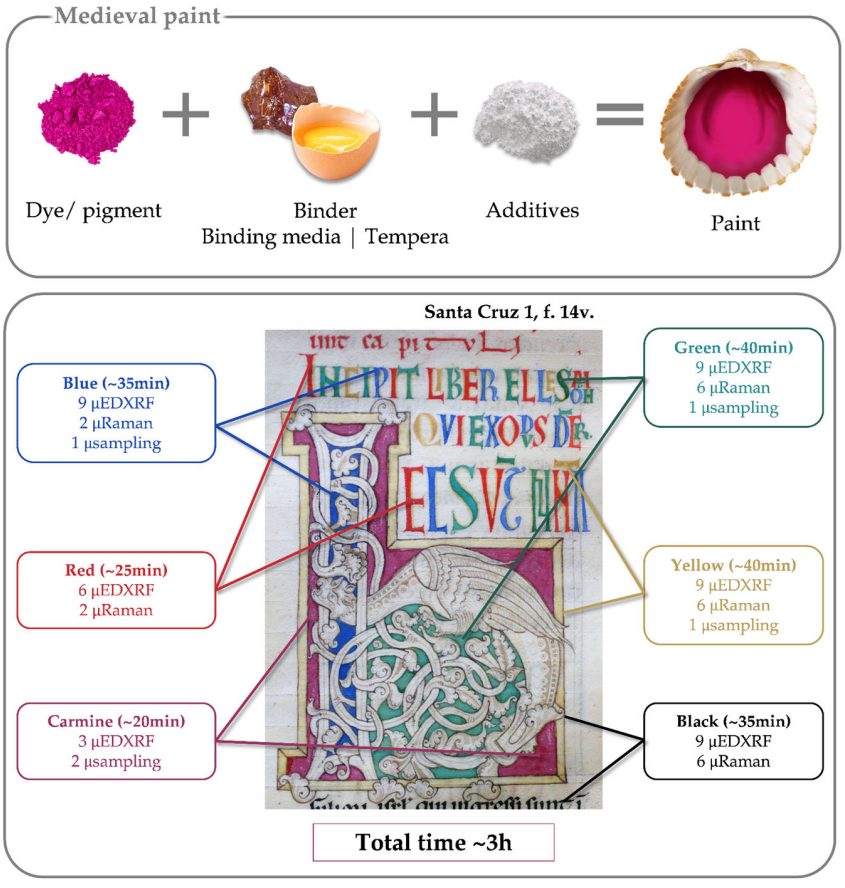

Figure 2. The medieval paint formulation comprises the dye or pigment, the binder, and additives (**top**). The average time for analysis of this initial in situ was 195 min, more than 3 h. The microsamples would have taken 90 min.

Paints are first analyzed by optical microscopy to understand how the final color is built up, to detect possible degradation phenomena, and to select the color paints that

will be subjected to more detailed characterization in the laboratory in what concerns the colorants, binding media, and additives. After examining the illuminations under the microscope, we began the molecular analysis of the color paints and inks. Given the complexity and value of these materials, we usually interface the analytical techniques with a microscope to study the micro-samples. This enables us to examine areas on a micrometer scale, with a micrometer (μ) one thousand times smaller than a millimeter (as in millimeter).

Our analysis involves a combination of elemental and molecular spectroscopic techniques and constant comparison with historically accurate reconstructions to optimize the information acquired; see Figure 3. In the case of inorganic-based pigments, microX-ray fluorescence (microXRF) allows us to detect the elements present in these pigments, thereby enabling us to postulate an initial hypothesis for the colors [13]. In some instances, it even facilitates the semi-quantification of pigment mixtures through comparison with reference materials [23].

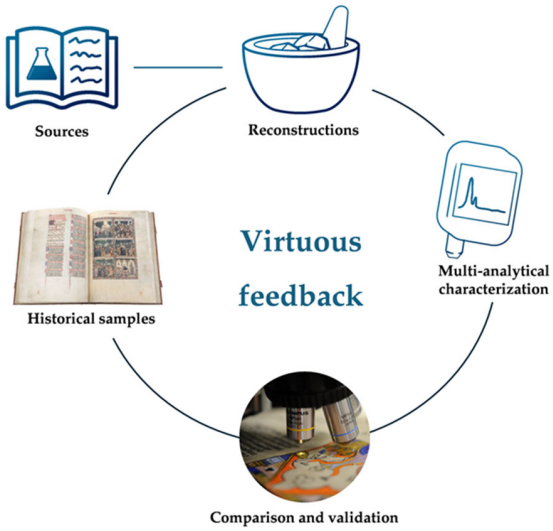

Figure 3. The feedback system for studying color in medieval illuminated manuscripts. The historically accurate reconstructions are made according to medieval written sources and are highly characterized by an analytical approach. The information obtained is used to understand better the historical colors and objects at the molecular level.

Raman microscopy (microRaman), Fourier Transform Infrared spectroscopy (microFTIR), emission fluorescence spectroscopy in the visible (microspectrofluorimetry), and Fiber Optic Reflectance Spectroscopy (FORS) in the UV–Visible region are not just individual techniques but a powerful ensemble [1,24–26]. They comprehensively characterize colorants in medieval manuscripts, whether organic or inorganic [5,15,18].

During the in situ investigation of a medieval codex, the first screening is carried out by FORS and microXRF, the latter of which indicates the colorants and extenders present and allows for the initial quantification of these elements; moreover, the 70 μm spot size offered by microXRF enables us to obtain data on the distribution of a certain paint color throughout the manuscript. Handheld Raman spectroscopy is now particularly effective for materials identification in increasingly complex formulations [21]. Combined with the crucial information on optical microscopy, this allows for selecting the micro-samples that will be studied by microFTIR, microRaman, and microspectrofluorimetry. The micro-samples are collected under the microscope using the following micro-tools from Ted Pella®: a micro-chisel no. 13603 attached to a micro-graver oval no. 13611. MicroRaman and microspectrofluorimetry allow high spatial resolution (1–5 μm spot) to analyze diverse paint components separately. Microspectrofluorimetry was paramount for fully characterizing the dyes and lake pigments present. If necessary, combining SERS

(Surface-Enhanced Raman Spectroscopy) in a small selection of micro-samples corroborates the main dyes present [18–20].

2.3. How to Preserve the Micro-Samples

How do we protect and preserve these extremely small micro-samples, invisible to the eye? This is indeed a crucial point that we have been working on. We preserve them in polypropylene cabinets and keep them on glass slides at 20 °C. Possibly, we could improve these conditions, and a more open debate could be launched among interested parties. We consider more details next. Micro-samples are stored on microscope slides with a single cavity and covered with a microscope glass slide. They were closed with tape (3M magic tape) and used as sample holders. In situ, spectra are collected directly from the sample by opening the cover. These sample holders are stored in a microscope slide tray cabinet in a dust-free enclosure. The cabinet's outer shell is white polypropylene, and the tray rails are polystyrene.

2.4. The Next Steps in the Characterization of Medieval Illuminations

The multi-analytical characterization used until now has been essential for studying illuminated manuscripts. Nonetheless, we have been focused on implementing new techniques or improving existing ones, resulting from the constant innovation in the scientific field.

Improving handheld techniques and the information acquired is an example of this innovation that proved fundamental for studying manuscripts [12,27]. Recently, by applying a handheld Raman instrument, we proposed the molecular color palette for four manuscripts belonging to Alfonso X, the Learned [28]. Not only was it possible to identify the colorants used, but it was also possible to disclose part of their formulation by identifying the additives. The detection technique used by the instrument, the orbital raster scan (ORS), allows the acquisition of information on a larger sample area, which is essential for multicomponent formulations, and simultaneously reduces the risk of heating the surface and damaging the paint [29]. Another advancement in Raman spectroscopy has shown great potential for future studies in illuminated manuscripts, i.e., Surface Offset Raman spectroscopy (SORS) [21,28,30,31]. It permits the differentiation between colors acquired by mixtures or by layered paints, which are common practices in these objects, and it has been evolving from benchtop counterparts to handheld instruments.

Furthermore, synchrotron techniques have the potential to significantly enhance our understanding of medieval colors, as discussed in Section 5. While traditional techniques enable us to identify the materials, deep-UV fluorescence spectroscopy has proven to be a valuable tool in characterizing the heterogeneity of the samples [32]. Our recent discovery that the makers would manipulate not only the formulation, i.e., the recipe, but also the mixing of the materials, leading to different tonalities depending on the size and typology of the grains, is a significant finding with practical implications. This research field requires us to consider that their stability relies on the materials and formulation used and how the paint was processed, which can guide conservation and restoration efforts.

3. Modern and Contemporary Materials: Synthetic Polymers in Museum Collections

3.1. Synthetic Polymers in Collections

The significant developments of the chemical industry in the mid-nineteenth century led to a wide range of semi-synthetic and synthetic polymeric materials in the first decades of the twentieth century [33]. These replaced natural materials and were combined to generate new products with improved properties [34]. The introduction of synthetic polymers can be found in several formulations in different objects such as paints, textiles, films, and three-dimensional plastic objects (thermosets, thermoplastics, and elastomers). The historical relevance of synthetic polymers becoming one of the most relevant material classes in modern and contemporary times is reflected by the presence of daily life objects

and art artifacts made of plastics as an integral part of modern art, design, science, and technology museums worldwide nowadays.

Even though plastics have a recent history compared to other historic materials found in museums, they have a relatively short life expectancy, in contrast to a common belief of their everlasting stability. If one combines the enormous variety of plastic formulations and the wide range of aging behaviors, then it is clear that the heritage community faces a difficult challenge in terms of conservation. Efforts dedicated to researching the materiality of plastic-based collections and their preservation started in the 1990s with the succession of conferences dedicated to the degradation, conservation, and production technology of plastics [35–38], the foundation of the ICOM-CC "Modern Materials and Contemporary Art" Working Group, the survey of plastic collections by museums for assessing their conditions to determine conservation priorities [39–41], and the establishment of projects dedicated to develop strategies to preserve plastics in collections and archives in Europe [42–44] and outside Europe [45–47].

3.2. Investigation of Synthetic Polymers at the Deutsches Museum

The Deutsches Museum (DM) is one of the oldest and largest museums of science and technology in Germany. It contains more than 120,000 artifacts, of which ca. 38,000 are made (or contain parts) of plastics, that are present in several collections (e.g., Chemistry, Physics, Medical Engineering, Music, Foto and Film, Telecommunication, Robotics, Informatics, Maritime Navigation, Aviation, and Space).

Scientific studies are fundamental to understanding the complex behavior of plastic-based materials [48], and the selection of suitable analytical instruments [42] and the development of tailored analytical methods is a growing topic. For this reason, a new conservation science department was established at the DM in 2014 to investigate plastics, mainly in the collection, using spectroscopic and chromatographic analytical methods for the following purposes: (i) identifying synthetic polymers and/or additives; (ii) studying their aging products and processes; and (iii) assessing the effectiveness of preservation methods.

To respect the historical and material integrity of the collection, the analytical study of the objects prioritizes the use of in situ methods (i.e., methods that require no sampling). In this section, the benefits of micro-sampling and subsequent deep investigation in the laboratory, as well as the creation of mock-ups and their systematic study along with their comparison to original samples/objects, will be presented.

3.2.1. The Identification of Synthetic Polymers and/or Additives

Thanks to FTIR-ATR (FTIR attenuated total reflection), synthetic polymers present in radios dating from the 1930s to the 2000s were successfully identified. This study aimed to develop a classification scheme for estimating the plastic type without analytic tools since most museums cannot access analytical instrumentation. The time of production of the objects, archival research on their manufacturing process, the range of plastics used at that time, visible production features on the plastic parts, and their flexibility, opacity, and deterioration patterns were taken into account to suggest the most probable plastic present. The spectroscopic investigation corroborated the plastic identification and denoted a material evolution in casings, dials, handles, and printed circuit boards (from thermosets to thermoplastics and elastomers), contributing to the history of the technology of such objects (Figure 4). It also verified that the historical literature mentioned the wrong plastic in two of the six case studies [49]. The FTIR-ATR measurements were conducted without collecting samples when good contact between the diamond crystal and the object was ensured (the pressure applied was also safe for the historical object). However, micro-samples were collected mainly to analyze the less accessible areas (e.g., inner parts). These micro-samples were documented and preserved in the DM laboratory (adapting the description in Section 2.3.) due to their potential to be used in future research by other analytical methods.

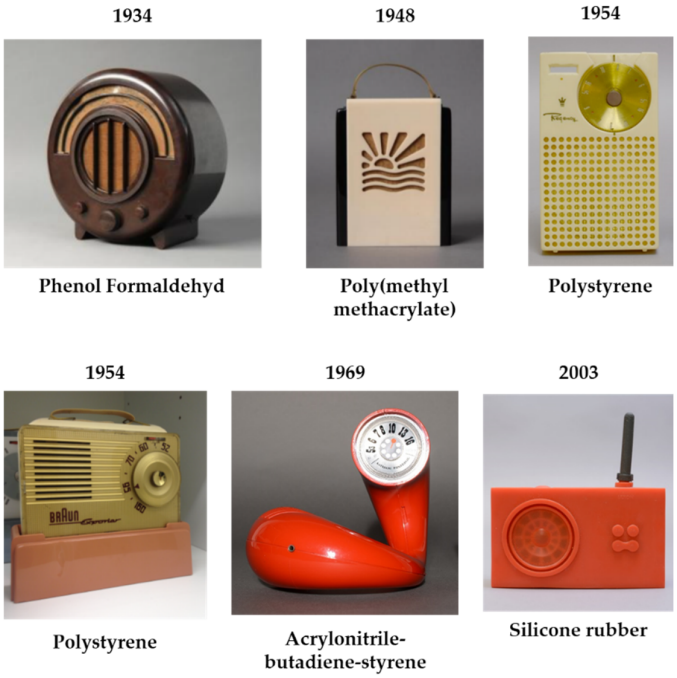

Figure 4. The range of synthetic polymers (thermoset, thermoplastics, and elastomer) identified in radio casings from 1934 to 2003 by FTIR-ATR [adapted from [49]]. Most radios courtesy of Die Neue Sammlung—The Design Museum, Munich.

Further studies used FTIR-ATR to identify the polymer(s) of plastic objects in museum collections [50–53]. FTIR-ATR also supported the development of non-analytical criteria for conservators and/or curators to estimate plastics present in museum collections [54,55], proving to be a reliable and relatively fast method to identify the polymer composition. The probable identification of plastics can be achieved by answering questions related to the optical and physical features of the objects, the presence of production markings, and signs of degradation/damage.

Sampling and analytical methods such as Gas Chromatography/mass spectrometry (GC/MS) are typically implemented if information about the plastic formulation ingredients < 3% (e.g., additives) is required, as other in situ methods such as FTIR or Raman spectroscopic only detect concentrations above this amount [42]. After being studied using spectrometry-based methods, the sample cannot be recovered. As an example, Thermodesorption-Gas Chromatography/mass spectrometry (TD-GC/MS) was used to characterize additives in historical cast sheets of poly(methyl methacrylate) (PMMA) used by artists and from industrial swatches [56]. This method required ca. 100 µg micro-samples. The identification of additives and an inquiry about the used industrial production methods helped to estimate their impact on the stability of the PMMA samples to photo-oxidation. The presence of more plasticizers, the use of recycled monomer, and the lack of a post-polymerization step were correlated to higher degradation extents in the PMMA samples.

3.2.2. Study of Deterioration Products and Aging Processes: The Example of Discoloration

Plastics can suffer from extensive degradation depending on the formulation, production/processing methods, and exposure to environmental factors (light, humidity, temperature, and pollution) [41,57]. Studies focused on the discoloration of heritage plastics in conservation science are limited [58].

ß-naphthol pigment reds, substituted 1-arylhydrazone-2-naphthols, are one of the first pigment categories used in the coloring of plastics [59,60], and problems related to their fading in plastic artifacts are well-documented [61,62]. Two red plastic lids presenting different discoloration stages made of polyethylene (PE) from the 1950s–1960s used for food containers from a private Portuguese collection mass-colored with PR 48:2 and PR 53:1 were

subjected to photo-oxidative artificial aging to investigate their photo stability [58]. Because the discoloration is ruled by the chemistry of the possible interaction of the formulation ingredients within the plastic (i.e., polymer(s), colorant(s), and additive(s)), this research aimed at investigating their individual light susceptibility and combined effect. To do so, non-colored and additive-free PE samples, net pigment powders, and colored PE samples of historical plastic lids were artificially aged ($\lambda \geq 300$ nm), and their molecular changes were followed through FTIR-ATR and GC/MS. The same plastic specimens were used to monitor the aging via FTIR-ATR without sampling, while ca. 200 µg of samples by EGA-MS and TD-GC/MS and ca. 100 µg by Py-GC/MS were analyzed at different irradiation times. This experimental procedure allowed us to reliably monitor light-induced changes through in situ FTIR-ATR and obtain full disclosure of the degradation progress using mass spectrometry-based methods at specific irradiation times. Even though original plastic artifacts were sacrificed, the insights collected by these methods were significant for understanding the PR 48:2 and PR 53:1 discoloration in the lids. The more severe photofading of the historical samples suggested higher sensitivity to light of PR 48:2 and PR 53:1 in the plastic lids compared to the neat powders. This result suggests that the combined effect of the plastic ingredients may have a negative influence on the stability of the β-naphthol reds. The GC-MS methods were key in identifying phthalic derivatives, such as phthalic anhydride, 1,3-indandione, and phthalimide, in artificially aged pigment powders (Figure 5). These decay products, together with the identification of phthalic acid and phthalates in the irradiated solution of parent dyes [63], can inspire further mechanistic studies for the ß-naphthol reds.

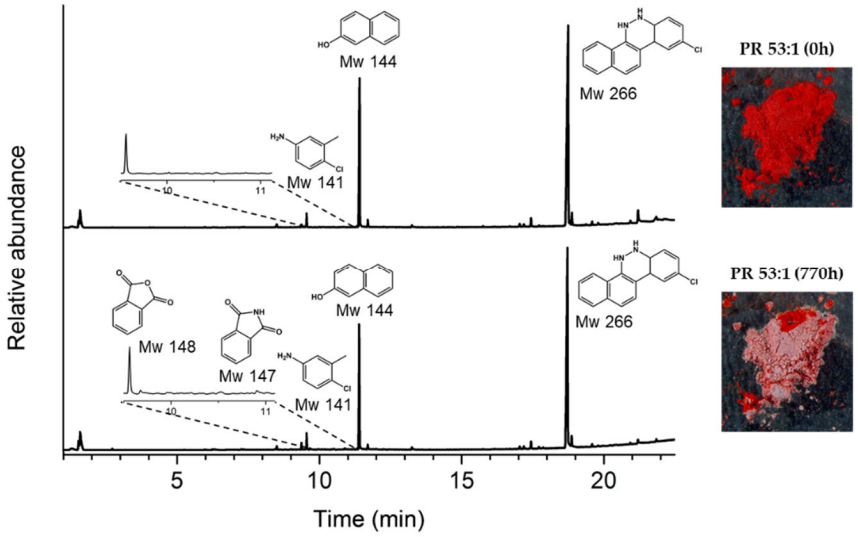

Figure 5. Normalized pyrograms of the net pigment powder PR 53:1 before (0 h) and after artificial light aging (770 h) and corresponding stereomicroscope images. Besides the main pyrolysis products (Mw 141, tR 9.6 min; Mw 144, tR 11.4 min; Mw 266, tR 18.7 min), decay products such as phthalic anhydride (Mw 148, tR 9.6 min) and phthalimide (Mw 147, tR 10.9 min) were detected [58].

A multi-analytical approach comprising in situ methods (colorimetry, µ-Raman, and FTIR-ATR spectroscopies) and the acquisition of samples analyzed by SEM-EDX, EGA-MS, and TD-Py/GCMS were crucial to investigating the composition of the elastomeric polyurethane (PUR) mask of the Japanese humanoid robot SAYA and understanding its degradation phenomena [64]. Ten years after its production, the androids' synthetic skin suffered from two large tears, stickiness, and extensive discoloration. Regions along the edges of the mask showed a particular color profile: yellow surface | pale pink core | yellow surface. Thanks to a selective sampling of a pale pink core (better preserved) in contrast to a yellow (sticky) surface, it was possible to detect the accumulation of UV stabilizer and phthalates on the surface, which, especially for phthalates (DINP and DEHP), caused a

widespread stickiness and the consequent attachment of dust particles. The degradation of the mask derived not only from the organic additives but also from the light susceptibility of the formulation: methylene diphenyl diisocyanate (MDI) PUR ether containing styrene-acrylonitrile (SAN). Furthermore, the white pigment titanium dioxide (TiO_2), present in both rutile and anatase crystalline forms, likely imparted a greater susceptibility of the elastomer to photo-oxidation due to the higher photochemical activity of anatase.

Both investigations highlighted the importance of integrating the information gathered from different analytical methods. The in situ techniques revealed differences in color and functional groups located in specific areas of the objects/samples, which allowed performing a precise micro-sampling. The analyses of those micro-samples by mass spectrometry-based methods were crucial to shedding light on the possible causes of discoloration.

3.2.3. Study of Preservation Methods

The Informatics' collection of the DM has several personal computers (PCs) that are yellowed. This is a typical degradation phenomenon occurring in several collections with objects made of acrylonitrile–butadiene–styrene (ABS) and styrene derivatives because these polymers are prone to yellowing due to photo-oxidation [65,66]. In a research study, historical plastic samples (2 cm × 2 cm × 4 mm) of a naturally aged ABS keyboard from the 1970s were cleaned by atmospheric plasma (for removing yellowed surface layers) and protected with a coating against UV radiation, consisting of TiO_2 nanoparticles immersed in tetraethyl orthosilicate (TEOS) applied by plasma. The durability of the coating was assessed by monitoring changes in the surface after artificially aging the samples ($\lambda \geq 280$ nm). Measurements by FTIR-ATR, profilometry, colorimetry, and the contact angle were performed before and after the treatments. This allowed us to conclude that the coating provided protection against light aging even though it was heterogeneously dispersed. In this sense, it could become a suitable treatment if its application procedure was improved and adapted for museums. A preventive conservation approach, i.e., by implementing filters for natural light and introducing light-emitting diodes in display cases exhibiting PCs, was considered the most suitable approach to preserving museum computer collections at the DM [67].

Several studies, also in part mentioned above, used larger samples of a real object to test the effects of preservation methods and assess their durability after exposure to artificial aging [56,58,67,68]. The preparation of mock-ups may be a valid alternative for investigation purposes to avoid extensive sampling and/or overcome the material heterogeneity of cultural heritage objects. The mock-ups should mimic historical materials as closely as possible in composition and processing, to relate their material changes (typically from an unaged to an artificially aged condition and/or after applying different treatments) to real behaviors. As such, the effects observed in mock-ups can support selecting the most suitable conservation treatment [69–71].

The chemical assessment of the effectiveness of storage conditions for celluloid 3D objects (3D-CN) [72] is such an example. Mock-ups deriving from commercial sheets with a specific formulation were processed by compression molding to obtain three-dimensional geometries that were thermohygrometrically artificially aged. The comparison of analytical data with historical objects highlighted that the mock-ups were representative of moderately aged artifacts [73]. However, the heterogeneous nature of celluloid alteration, i.e., the development of degradation gradients in thicker 3D-CN objects (>0.5 mm), made it necessary to apply a novel sampling technique [72,74], which selectively considered several depths for analyses from the surface to the core (depth profiling). By comparing the degradation gradients of moderately aged mock-ups and severely aged historical objects, it was possible to verify an inversion of their orientation in profile (Figure 6).

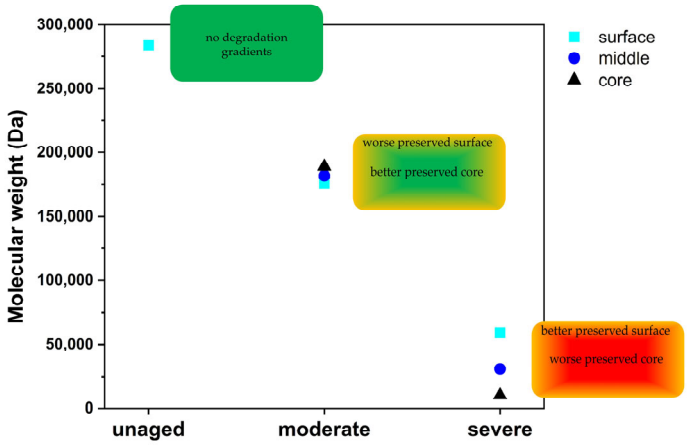

Figure 6. Molecular weight data of 3D-CN show that degradation gradients in depth profile are formed due to aging. The orientation of the gradient in moderate condition (more degraded surface than core) seems to inverse when 3D-CN reaches a severe condition (higher polymer chain scission in the core than at the surface) [adapted from [72,73].

The sampling strategy in profile was crucial to finding the correlation between the four different storage temperatures tested (+23 °C, +13 °C, +9 °C, −15 °C) and their impact on the chemical stability of the specimens, with the lowest temperature being the most effective. The molecular weight was the most sensitive parameter (compared to the camphor and nitrogen contents) to follow changes after artificial aging [73] and seven months of storage [72]. On the one hand, it was an advantage to investigate mock-ups because no ethical issues were faced during sampling, as the molecular chain length analyses required 5 mg of sample per measurement and depth. On the other hand, the mock-ups were processed from celluloid sheets with one formulation and processing method, which can be less representative of different celluloid plastic formulations present in museums. In the future, GPC analyses of mock-ups in depth profiles seem promising to systematically study the heterogeneous nature of 3D-CN degradation, i.e., the mechanisms that lead to spatial orientation changes in degradation gradients with increasing aging.

Above all, the preparation of mock-ups in heritage science studies can be considered a valid scientific approach for investigating materials by destructive analytical methods, even though the amount of testing variables is normally limited and funding is required for such investigation.

4. Modern and Contemporary Materials: Cellulose Nitrate in Museum Collections

In 1988, Rankin et al. highlighted the deterioration of cellulose nitrate sculptures by Antoine Pevsner and Naum Gabo. Pevsner's The Dancer (1927–1929) had yellowed, losing its intended transparency, while Gabo's Construction in Space: Two Cones (1927) was utterly fragmented [75]. This visual description of the artworks' conservation conditions raised awareness about the instability of cellulose nitrate and, more generally, plastics in cultural heritage. However, as Lemaire et al. noted, "chemical evolution is responsible for the degradation of physical properties. In weathering, there are no examples of physical aging without chemical modifications" [76]. While physical changes in artworks, such as yellowing and cracking, are evident to the naked eye, comprehending the chemical modifications necessitates multiscale analytical techniques. These methods, such as infrared, Raman, or luminescence spectroscopies, are crucial in understanding molecular degradation mechanisms, which is vital for developing effective conservation methodologies.

In the last ten years, analytical studies have expanded to using in situ Raman and FTIR portable and handheld spectrometers for analyzing plastics in cultural heritage settings [51,77–86]. The number of similar studies is expected to increase over time: due to the ubiquity and variety of plastics in 20th–21st-century society, there is a vast array of collections worldwide with different characteristics, either owned by large and well-funded

institutions or small collections with limited resources, which require characterization campaigns to identify the composition of their plastics, especially those of high degradation risk such as cellulose nitrate. Contemporary portable and handheld spectrometers allow cost-efficient, fast, and reliable analysis with good spectral resolutions and signal-to-noise ratios, detecting the polymers and the primary additives, such as plasticizers, fillers, or colorants. Furthermore, quantitative methods for assessing degradation can be developed. For example, using a portable FTIR-ATR device, Nunes et al. constructed calibration curves to quantify the decrease in the degree of substitution in cellulose nitrate and cellulose acetate [82]. This valuable information supports well-informed preventive conservation procedures. Molecular data from in situ instruments can be integrated into predictive degradation models and allow innovative tools for conservators to determine the lifetime of the artifacts, as demonstrated for cinematographic films in the NEMOSINE project [87,88].

However, these in situ techniques have key limitations for studying plastics' cultural heritage. Micro-analytical laboratory equipment typically offers superior sensitivity and spectral and spatial resolutions. This greater capability allows for the detailed analysis of the complex heterogeneities in plastics, which provides valuable insights into these materials' cultural significance. The critical role of artifacts' microscale heterogeneities in fully understanding the history of plastics was recently exemplified by an interdisciplinary and multiscale study on the composition of John Wesley Hyatt's billiard balls, made of cellulose nitrate, camphor, and ground bone [89].

The power of microscale analysis to detect lower concentrations of analytes is essential for plastics conservation studies. Polymers live as "chemical reactors", meaning that, during degradation, chemical groups are formed in very low concentrations [76]. Therefore, employing sensitive techniques to detect degradation at the earliest stages of chemical evolution is crucial. Traditionally, reactive intermediates and degradation products of cellulose nitrate have been characterized using FTIR and Raman spectroscopies [74,90–93]. However, there are spectroscopic techniques with better detection limits, namely, luminescence spectroscopy. Another approach to increasing sensitivity is utilizing synchrotron radiation, which offers high brightness and tunability across a wide range of wavelengths. Despite synchrotron techniques' significant potential for studying plastics, their application has been virtually nonexistent [94,95]. Synchrotron deep-UV photoluminescence micro-spectral imaging (DUV-μPL) was demonstrated to be a fundamental technique for studying cellulose nitrate-based plastics. Due to its extended wavelength range (180–600 nm), its sensibility (10^{-9} M), and high achievable spatial resolution (<1 μm), this technique was able to characterize and map, by combining spectral and spatial information, the submicrometer heterogeneous environments of cellulose nitrate artifacts related to degradation and manufacturing particularities. No degradation was observed to be induced in the samples due to the synchrotron excitation beam [32].

Certain organic components in very low concentrations may not be detected by FTIR or Raman (for components with concentrations below 5% w/w in addition to fluorescence background noise). Gas Chromatography/mass spectrometry (GC/MS) can be employed in such cases due to its detection limits ranging from nanograms (10^{-9} g) to femtograms (10^{-15} g). This technique has been extensively used to study cellulose nitrate heritage. It has proven effective in identifying many additives in cellulose nitrate artifacts, including acetanilide, glycerol triacetate, and diethyl diphenyl urea [50,93,96–101]. These additives contribute to the complexity of cellulose nitrate-based plastic matrices and influence the materials' lifetime. They carry historical information, as the formulations can be correlated with patents or industrial recipes, facilitating studies on dating and provenance. Moreover, GC/MS can be used as a quantitative technique by calculating peak area ratios between volatile compounds to evaluate the extent of degradation. Curran et al. demonstrated that furfural is a degradation marker for cellulose nitrate-based plastics using this methodology [101]. However, this technique consumes the samples, with methods for cellulose nitrate requiring between 50 and 500 μg of material. Given that a micro-sample can weigh as low as 0.1 μg, current GC/MS methods demand 500 to 5000 times more

sample material than molecular and elemental microscopy techniques, which, in addition, do not consume the sample. Therefore, the appropriateness of GC/MS methods should be carefully considered according to the artifact's cultural significance and the objectives of the characterization studies.

5. Conclusions and Perspectives

5.1. Investigating Medieval Colors and Modern and Contemporary Artworks

Our research significantly contributes to the field, delving into the multiscale heterogeneity of organic historical materials and showcasing an innovative approach. We commence by studying the colors in medieval manuscript illuminations and the importance of micro-sampling to minimize manuscript damage. The degree of usefulness and innovation allows us to assess the object's conservation condition and discuss practical conservation treatments, such as cleaning, stabilization, and restoration. As a starting point, we employ advanced techniques such as microRaman, microFTIR, microXRF, and microspectrofluorimetry to study precious micro-samples in medieval manuscripts, which are invisible to the naked eye and are only observable under a microscope. In institutions and museums, handheld techniques such as Raman and UV-VIS provide relevant and complementary data following microscope observation. Novel applications are discussed in Section 5.3.

This heterogeneity is also present in modern and contemporary materials, and our goal is to preserve these objects in practical conservation scenarios. Our research enhances our theoretical understanding and provides practical solutions for conservation. The diversity of plastics in radios from 1934 to 2003 using FTIR-ATR measurements showed the fantastic diversity of materials, complemented by micro-sampling whenever necessary. The reasons behind the degradation of ß-naphthol reds are also analyzed (one of the first pigment categories used in the coloring of plastics). The decay products studied by mass spectrometry-based techniques will allow for further mechanistic studies for the ß-naphthol reds. Even though ca. 200 µg of samples was damaged by EGA-MS and TD-GC/MS and ca. 100 µg of samples was damaged by Py-GC/MS, a high degree of usefulness and innovation was obtained. The yellowing of computers and active measures to slow it down are also discussed, being the preventive conservation approach based on implementing filters for natural light and introducing light-emitting diodes in display cases to preserve museum computer collections at the Deutsches Museum.

Most case studies prove that complementary information can be obtained by conjugating several analytical techniques, allowing researchers to comprehend the heritage system better. Due to a lower degree of intervention, spectroscopic in situ methods are often applied in the first step of the investigation, while chromatographic mass-spectrometric methods are kept for specific questions that the previous ones cannot answer. The interpretation of analytical results by a multidisciplinary team is an essential step in heritage science.

5.2. Historically Accurate Reconstructions and Mock-Ups: In Modern and Contemporary Artworks and Medieval Colors

Preparing mock-ups for plastic studies is a valid scientific approach to investigating materials using analytical methods. The mock-ups mimic historical materials as closely as possible in composition and processing to relate their material changes (typically from an unaged to an artificially aged condition and after applying different treatments) to actual behaviors. This strategy was fundamental to studying 3D celluloid because it deteriorates fast and develops heterogeneous degradation gradients during aging, which is hard to detect by the naked eye. Sampling in-depth profiles and performing quantitative mock-up analyses can support aging studies and selecting the most suitable conservation treatment for such sensitive polymeric matrixes. Reconstructing medieval colors is challenging; we have been doing it for the past 15 years [5]. This allowed us to improve our knowledge and to prepare reference materials with as much historical accuracy as possible, validated by their "closeness to the true value" of the historic material or artwork under

study. These reconstructions will allow advancing knowledge toward the conservation of medieval colors.

5.3. Novel Applications in Cultural Heritage: In Modern and Contemporary and Medieval Colors

UV/Visible photoluminescence spectral imaging using a low-intensity ultraviolet synchrotron has been extensively applied in biological studies, for example, in the DISCO imaging beamline of the SOLEIL synchrotron facility. Despite these synchrotron techniques' significant potential for studying the heterogeneity of organic historical materials, their application has yet to become virtually nonexistent. To study cellulose nitrate-based plastics, this research used synchrotron UV/Visible photoluminescence [32]. Due to its extended wavelength range (180–600 nm), its sensibility (10^{-9} M), and high achievable spatial resolution (<1 μm), it was possible to characterize and map the sub-micrometer heterogeneous environments of cellulose nitrate artifacts related to degradation and manufacturing particularities [32]. No degradation was observed in the samples due to the synchrotron excitation beam. This technique was also recently used to study three samples of lac dye colors in medieval monastic scriptoria without damaging the samples. The samples were recovered into their glass slides and transported from the Soleil synchrotron near Paris to Portugal.

5.4. Overview

In situ portable and handheld spectrometers have become practical and accessible tools for characterizing plastics. They enable the quick analysis of extensive collections, particularly those made of cellulose nitrate and at high risk of degradation. These methods are well-suited for collections where minimizing sample damage is crucial and cost-effective solutions are necessary due to resource limitations. However, portable/handheld methods have sensitivity and spatial resolution limitations compared to laboratory-based micro-analytical techniques. Advanced techniques such as synchrotron luminescence spectroscopy can detect chemical changes at very low concentrations and with great spatial resolution. This makes them particularly useful for studying the early stages of polymer degradation and material heterogeneities. Future studies on the conservation of plastics should consider synchrotron techniques more often.

When comparing the sample sizes required for different analytical methods, in situ techniques have the advantage of not requiring sampling or, when required, very low quantities that can be fully recovered. On the other hand, techniques like GC/MS, with their unparalleled sensitivity, are highly effective for identifying additives and degradation markers, even though they require much larger sample sizes. This difference is important in the context of cultural heritage, where preserving the integrity of the original material is crucial. As GC/MS continues to evolve, new methods that require smaller sample quantities will promote its increased applicability in conservation science.

Looking ahead, integrating molecular data from in situ techniques with predictive degradation models represents an exciting avenue for innovation. This approach, already demonstrated in projects such as NEMOSINE, will enable conservators to better estimate the lifetime of plastic artifacts and implement more informed preventive conservation measures. Future developments should focus on increasing the sensitivity and resolution of portable instruments, expanding the use of synchrotron-based methods, and reducing sample size requirements for techniques like GC/MS. These advancements will enhance our ability to preserve and understand cultural heritage overall.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/heritage7100259/s1, Section SM1.

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