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Material characterization in the identification of unknowns

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Abstract

Materials characterization methods are widely used in many fields, such as in determining material properties when selecting materials to be used for a wide variety of purposes, such as building construction; aircrafts; and machines; or being used in application such as failure analysis to determine how a part failed and how it can be prevented in the future. Another application of materials characterization techniques that is less mentioned, however, is their use in identifying the identity and history of a material. This review seeks to explore this application of characterization methods, describing both how the methods are used, and the results obtained, with special focus on optical microscopy, used to examine the surfaces of structures, and various spectroscopies, used in examining various properties such as composition, crystal structure, etc.

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1. Introduction

The use of materials characterization methods in identifying the unknown aspects of a material can serve many somewhat unexpected purposes. For example, by learning the composition of a material used by a certain people in a period in the past, information can be gleaned on how their society functioned by how they used their natural resources. Another application is identifying unknown illegal substances, then being able to use that identification to trace the substance back to try to find their source.

As for the methods used in such applications, spectroscopy and microscopy techniques are used the most often. Spectroscopy can reveal elemental and structural details, which are obviously very useful in identifying a material, while microscopy can show surface details that give information on what processes the material has experienced.

This review will explore the application of microscopy and spectroscopy in three papers, presented by Zerboni et al, Galli et al, and Sero et al. In each paper these methods and their findings were the central focus, giving information on the origins of the examined materials and what processes they had been through.

2. Characterization methods in uncovering the history of rock samples

In the paper by Zerboni et al, rock samples from the region of the Sultanate of Oman were examined. These samples were of interest because they held rock art carvings that potentially dated back to the paleolithic era. Their examination could aid in understanding the weathering processes the rock had undergone which could be useful in the preservation of the carvings. The major methods focused on this paper were scanning electron microscopy (SEM), polarized microscopy, and confocal laser scanning microscopy (CLSM), and further characterization was performed through x-ray diffraction, electron dispersive x-ray analysis, and accelerator mass spectrometry radiocarbon dating.

The primary findings of the polarized microscopy and SEM were the formation of several features such as alveolar micro-voids and depressions caused by the dissolution of materials such as limestone and micritic mud, as well as dust films covering the limestone, as well as intergranular spaces filled by varnish materials [1]. The additional examinations done in this paper support the findings of the microscope examinations. The electron dispersive x-ray analysis helped to identify the elemental character of the various features, such as the varnish materials, while the x-ray diffraction was done on powdered samples of the varnish to show even distribution of the mineral phases within the varnish. Additionally, confocal laser scanning microscopy with fluorescent staining was conducted on the samples and identified various cells in biofilms in the rock samples. The main findings of these analyses were that there were clusters of cells growing in the rock that followed the fissures and cracks, most of these cells were metabolically inactive, and a thin layer of organic materials was found covering the rock surfaces [1].

The overall conclusion drawn by this paper was a timeline of events that occurred to these rock samples. Limestone dissolution started first, followed by the formation of voids that were filled in by the dissolution of rock varnishes. The dust films were likely caused by wind conditions, whereas the dissolution processes required an abundance of water, and promotion by microorganisms. This gives insight to the previous meteorological conditions of the area, as the oasis of Salut had to be wet in the past for the dissolution to occur, and its current arid state could have led to accretion of the dust films. The formation of the rock varnish is credited with the preservation of the rock art in these boulders. However, the study also notes that surrounding boulders that were examined that did not have preserved rock art also show similar structures. This suggests that these boulders may also once have had rock art, but were not as well-preserved by environmental factors and eroded away over time. In this way, by characterizing the rocks of the area, some aspects of history can be inferred, even if it is not able to be observed.

3. Characterization methods in the analysis of a painting

The second paper examined in this review, by Galli et al, also delves into learning about history through material characterization. In it, various regions of the painting "The Holy Family with St. Anne and the young St. John" by Bernardino Luini are examined using optical microscopy, x-ray fluorescence (XRF), and fiber optic reflectance spectroscopy (FORS) in order to better understand the composition of the painting, giving potential insight as to the painting methods of the time. As an aside, this study also sought to explore optical microscopy's use in painting characterization, but this aspect does not relate to the review, so it has been mostly omitted.

The study selected several regions on the painting to analyze, all of which were various flesh tone regions. The microscope images of these regions were then passed through filters and categorized based on RGB data through a mathematical process wherein they were mapped into hexcone cylindrical space, ultimately being assigned values using hue, saturation, and value principles, "hue" describing the "main color" of the pigment, "saturation" being the prevalence of white tints, and "value" being the prevalence of black tints [2]. The equations used for these purposes have been omitted, as they do not contribute to the discussion of the characterization findings.

For the XRF data, spectra were generated where peaks corresponded to chemical elements present in the samples, and the intensity reflecting the amount. The chemical elements were identified from the spectra using an algorithm. FORS data was handled in a similar manner. However, the data was not as clear-cut because FORS primarily being used in identifying pigments, and most of the pigments in the samples were similar flesh tones.

By relating the spectra peaks of XRF and FORS with the assigned values of the optical microscopy data, this study found an interesting link between these data sets, suggesting that optical microscopy data may be more useful in characterization studies than as a mere aside. More pertinent to the topic of this review, however, is the findings made by the elemental analysis on the pigments of the painting. This study found that the artist Luini used vermillion as the base for the flesh tones in this painting, layering it with lead white, ochres, and lakes to produce the desired colors [2]. This conclusion was reached by the presence of lead, which corresponds to lead white, and mercury, being characteristic of vermillion. Additional elements include iron and potassium, unique to ochres, and calcium and strontium, common in preparation layers in painting. Also notable are the absent elements characteristic of other common pigments, such as copper for verdigris, showing that these common pigments were not used. Finally, optical microscopy revealed other structural features useful for identification, such as green inclusions with morphology and color corresponding to green earth pigments. This wealth of information revealed how painters of the time created their colors, as well as some techniques they used. This analysis relates to history in an interesting way, by showing that Luini, as a member of Leonardo da Vinci's circle, used similar techniques and materials in creating his colors as da Vinci, demonstrating the wide cultural effect of da Vinci's work at the time.

4. Characterization methods in the investigation of an unknown adulterant

The third paper examined, by Sero et al, used desorption electrospray ionization-high resolution spectrometry (DESI-HRMS) in conjunction with Kendrick mass defect (KMD) analysis to examine an unknown product in order to identify an additive causing it to exhibit high levels of activity, causing environmental harm. The product presented for examination was a phytosanitary product that had been dumped and caused environmental harm, likely due to the presence of an adulterant [3]. Without any information on the identity of the product or the adulterant, a broad mass spectrum was generated using DESI-HRMS. Desorption electrospray ionization-high resolution spectrometry involves spraying a sample with an electrically charged mist to ionize it, then running those ions through a mass spectrometer, allowing for data collection under atmospheric conditions with relatively minimal sample preparation and destruction. Because the full mass spectrum from the sample had a large collection of complex peaks, modified KMD analysis was applied with ethylene oxide as the repeating unit instead of the usual CH_2.

Using the distributions generated after applying KMD analysis, the presence of a single homopolymer in the sample was confirmed, and the elemental composition was narrowed to a range of $C_{0-100}H_{0-200}N_{0-5}O_{0-20}$. The ion with the smallest mass-to-charge ratio was used for putative identification, making the polymer $C_{10}H_{22}O(EO)_n$. Other ions and potential polymers were identified as well, but the above polymer was deemed the primary component because it fit the high density of the examined phytosanitary product. Its chemical inertness, however, meant that the search for the activity-promoting adulterant had to continue.

Using other peaks in the mass spectrum, potential metal ions were identified and narrowed down using earlier constraints, such as the elemental composition mentioned earlier, to isolate to a few organotin (tin-containing) ions. Additional, more focused DESI-HRMS scans were done on the ions of interest within the sample, narrowing the potential adulterant to a few triphenyltin compounds. Samples of these compounds were bought and analyzed separately, showing spectra that matched with the peaks in three sample, further supporting their presence.

Finally, to confirm the presence of these ions, ultra-high performance liquid chromatography coupled to high-resolution mass spectrometry was performed, with peaks once again corresponding to what was shown in the sample. As an aside, this data also indicated a potential interconversion between various triphenyltin compounds within the sample. The toxicity levels of tin in these compounds points to this being the adulterant causing the high activity levels.

This study demonstrated the value of characterization methods in identifying unknowns. The addition of the adulterant to the phytosanitary product can be seen as a process that the product underwent at some point in its history. By understanding what sort of compounds were actually put in, it can potentially help to trace when the product may have been contaminated, and also by what party, helping in prevent future environmental harm.

5. Conclusions

Throughout this review, characterization methods, especially microscopies and spectroscopies, have been shown to help glean information in rather unexpected ways, demonstrating how useful these methods can be, even in applications where one would not expect them to be. By showing the processes that materials have been through, supporting evidence can be generated for a wide variety of conclusions, such as those regarding history, or environmental harm, as demonstrated by the examples in the review, showing that these basic analyses are useful for almost any study. Without microscopies, for example, it would be much more difficult to see how materials in a sample are arranged, such as in the examination conducted in the paper by Zerboni et al. While other methods may have been able to identify the materials present, SEM images are immensely useful in seeing how they are laid out. Another example of this from the same paper would be how the polarized microscope images were useful in quickly showing the presence of voids, indicating the void-formation process had occurred. Spectroscopies are equally important and useful; without x-ray fluorescence in the second paper, it would have been impossible to actually identify the compounds in the paint, so no historical information could have been gleaned. This is even more so the case in the third paper, wherein without spectroscopy methods, analysis could not have been done at all, since the sample was completely unknown and could not be tampered with for fear of unexpected reactions with the potential adulterant of interest. Overall, these methods are essential in many applications, alongside other characterization methods not examined in this paper.

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Conflict of Interest

The author has no conflict of interest.

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