

Non-destructive analysis and testing of museum objects: An overview of 5 years of research

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Abstract

This paper gives an overview of research in or associated with the pan-European network COST Action G8, which aims at achieving a better preservation and conservation of our cultural heritage by increasing the knowledge of art and archaeological objects through advanced chemical and physical analyses. The paper is focussed on the use of various analytical techniques for the examination of cultural heritage materials and includes research examples on painted works of art, ceramics, glasses, glazes and metals. In addition attention is drawn to advances in analytical instrumentation, for example the development of portable techniques to perform analyses on site, and to the need for collaboration between people directly involved in the field of cultural heritage and analytical scientists.

Introduction

The conservation and preservation of our cultural heritage is one of the main concerns within Europe today. Its physical is deteriorating faster than it can be conserved, restored or studied. Assets are being lost, or are at risk, through natural processes of decay (sometimes accelerated by poor environmental control), environmental disasters (sometimes exacerbated by human activity), the direct effects of enhanced public access (without commensurate conservation measures), conservation/preservation procedures whose long-term effects were and are not understood, simple negligence, looting and war [1,2].

Advanced analytical methods and techniques are an essential prerequisite in this field as they provide the means to understand the objects under investigation. Through the identification of materials and processes, we can reach back through time and develop a deeper understanding of the craftsmanship and technology that was used. Advanced analytical methods also allow us to perform authenticity studies or contribute to the development of simple diagnostic techniques necessary for practical applied conservation [1,2]. The analytical methods used in this field of research are identical with those

used at the cutting edge of modern science [3– 22]. Techniques developed for advanced physics, chemistry and biology have a commonality of application to both ancient and modern materials, since problems encountered in both the advanced technology and cultural heritage areas are similar. However, there is one essential difference between the analysis of ancient and modern materials—an art object or ancient artefact cannot be replaced, and the consumption or damaging of even a small part of it for analytical purposes must be undertaken only where vital data cannot otherwise be obtained.

Depending on the information required, one might use a combination of truly non-invasive techniques (i.e. those which do not require a sample to be removed from the object, and which leave the object in essentially the same state before and after analysis), micro-destructive techniques (i.e. those which consume or damage a few picoliters of material and which may require the removal of a sample) and non-destructive techniques (i.e. a sample or complete object can be re-analyzed (with another technique) for further examination). The distinction between these techniques and types of analyses is of particular importance in the conservation field. Nevertheless research scientists generally use the term “non-destructive” for any of the above-mentioned analysis methods [23]. In all cases, however, one should aim at the maximization of information and the minimization of the consumed volume.

This paper gives an overview of research in or associated with the pan-European network COST Action G8. COST is an EU initiative that allows the coordination of nationally funded research at a pan-European level and its activities are based on so-called actions which are networks on a specific topic covering basic and pre-competitive research. Action G8 is one of these networks and has 24 member countries. Its first goal aims at achieving a better preservation and conservation of our cultural heritage by increasing the knowledge in art and archaeological objects through chemical and physical analyses [2]. Furthermore Action G8 aims at creating a Europe-wide environment, in which people directly concerned with the maintenance of our cultural heritage (i.e. art historians, archaeologists, conservators and curators) and analytical scientists (i.e. physicists, chemists, material scientists, geologists, etc.) can exchange knowledge. The multidisciplinary community of action is essential as in the current economic climate it is extremely difficult for museums to develop new analytical methods or techniques. The need for collaboration with experts in state-of-the art analytical instrumentation is therefore very high and can tap-in to sources of knowledge and sophistication

of equipment, which would otherwise be impossible in the small conservation and science groups in museums.

In what follows the examples of research activities have been classified according to the type of material studied. Reading through the various examples, it should be kept in mind that in general the solution to any cultural heritage problem rarely depends on the application of a single technique, even though it may not be always explicitly mentioned. In addition there are many other analytical techniques commonly used in the field, which are not mentioned here.

Painted Works of Art

Paintings, frescoes, miniatures and illuminated manuscripts are an inherent part of our cultural heritage. The pigments used in these objects, including their spatial distribution, are characteristic for the period in which the art object was made, their provenance and, in most of the cases, the individual artist. Microscopic and molecular information about the nature and the distribution of pigments can therefore contribute to the answering of technical art historical questions, such as the deduction of the original appearance of the object, painting techniques, authenticity and the establishment of the chemical and physical conditions before conservation and restoration [24]. The latter is necessary, especially when deciding upon correct treatment methods to conserve or restore the artifacts.

Several elemental analytical methods are currently exploited for the analysis of painted works of art, including X-ray fluorescence (XRF) and particle induced X-ray analysis (PIXE), while methods, such as Raman, infrared (IR), X-ray diffraction (XRD) and static secondary ion mass spectrometry (SSIMS) can deliver specific molecular information. The latter is especially useful in the analysis of paint layers which are applied on top of each other or when a single paint layer contains several pigments.

The fact that analyses need to be done in a non-destructive and even more so in a non-invasive manner is extremely important here as removing samples is in most cases unacceptable. In that regard it is not surprising that XRF is an extensively applied technique in this field of analysis. For example Sközefalvi-Nagy et al. describe the use of titanium elemental mapping of white spots on paintings to date or authenticate the painting [25]. Analyses were performed by laying the paintings horizontally and positioning the X-ray beam by help of a

removable “aiming pin”. The method is based on the fact that titanium dioxide white (TiO_2) has only been available since 1920. However the decision is not always as simple since there are other frequently used white pigments such as barite (BaSO_4), zinc white (ZnO) or chalk (CaCO_3).

By no means all pigments can be classified by elemental analysis especially when dealing with pigments which contain the same elements but have a different chemical formula. In this regard obtaining molecular information of the compounds becomes crucial. The latter refers to specification of the local composition of a sample in terms of molecules rather than elements. Depending on the analytical methodology used, the oxidation state of an element, the presence of specific bonds, or the entire molecule as a whole is characterized. In a study by Hochleitner et al. [45] the combination of XRF and XRD was used to establish a database of commonly used inorganic pigments. Analyses were performed on commercially available powder samples. Results showed that the combination of both methods enhanced significantly the potential for obtaining results as most of the pigments could be distinguished by their phases. Here, in a similar way to XRF, synchrotron radiation X-ray diffraction (SR-XRD) is rapidly gaining interest in the field. In a study by Dooryhee et al., for example [46], SR-XRD is used to examine the pigments of a Roman wall painting. The joined elemental and mineral maps are able to mimic the major features of the painting. Moreover, different structural phases made of common atomic elements are differentiated and the textures and graininess can be measured and related to the artist’s know-how.

Raman microscopy has perhaps emerged as the most widely used molecular technique for pigment studies [16]. In a similar way to XRF equipment, instrumental developments have led lately to the availability of A-Raman instruments. Kendix et al. [47] used such instrument for the study of architectural paint to date wall paint from the “Landhaus Bauer”, a country house in Hamburg created by the Danish neo-classical architect C.F. Hansen. The results were compared with traditional XRD techniques and show a good agreement. Other studies including A-Raman include the analyses of mural paintings [33,48–50], paintings [51–53] and drawings [54–56]. The past few years, also mobile fiber-optic-based Raman instruments have been available on the market. They offer a means to avoid destructive sampling and eliminate the need to transport artifacts for spectrochemical analysis [57].