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Physics and heritage / Physique et patrimoine

# Foreword

There is today a strong interest in the cultural heritage, not only because it supports the tourism industry, but also because large fractions of the society require improved access to past and present human activities. In addition to uncovering the past, there is a need to understand the knowledge and the skills associated with objects, as well as to preserve them for the future generations. Multidisciplinary investigations are thus currently performed by curators, conservators, geologists, chemists, and physicists. These inclinations towards cultural heritage are attested, for instance, by the publication of several "Actualité Chimique" issues (no. 312, 313 and 318 of the 2008 journal of the French Society for Chemistry) or by two recent events linking physics and art, the "Light – colour: dialogues between art and science" exhibition in Paris [1] for the "World Year of Physics" that moved then to other French cities, and the "Arphystic festival" that took place in Lille [2].

To study cultural heritage objects, specific analytical techniques have been implemented; most of them derive from physics. Multi-disciplinary and multi-scale examinations of objects are a prerequisite to any detailed investigation. This starts with historians and curators who, in addition to direct visual observation, are helped by the use of various electromagnetic radiations such as infra red, ultra violet, X-rays, etc. The radiography of paintings has been performed more than 10,000 times since it began in the 1920s in the laboratory located in the Louvre Palace. Beyond infra red ($\sim$2 μm wavelength), terahertz spectroscopic imaging ($\sim$100 μm wavelength) is now in development [3]. These radiations aim at revealing features (structure, underdrawing, etc.) inside artworks, covered by surface layers.

Resulting from macro/meso-scopic examinations, many questions are often raised concerning the origin and the processing of the materials, the alteration of the object, the date and the know-how of manufacture, etc. Various techniques dealing with the electrons and the nuclei are used in order to determine detailed characteristics of the materials, such as chemical and isotopic compositions, atomic arrangements in molecules or in crystals, lattice imperfections, etc. Dating past events is fascinating; it has become a common practice in the middle of the 20th century thanks to the development of the nuclear physics that is involved in most dating techniques. Applications to cultural heritage studies are useful mostly for the past 30–50,000 years and, exceptionally, for older times. For such a time span, radioactive $^{14}C$ is particularly suited (the $^{14}C$ half life is 5730 years) to date organic materials left by living species when they stop being in chemical equilibrium with their environment, after their death. The amount of $^{14}C$ is directly related to the time elapsed after the death of animals or plants. It requires the measurement of $^{14}C/^{12}C$ ratios less than $10^{-12}$ that is currently carried out by accelerator mass spectroscopy (AMS) [4]. For instance, in a study concerning the disappearance of people from Greenland around 1500, the change of diet composition with time ($^{14}C$ dating), from terrestrial to marine food, was revealed by the concentration of the stable isotope $^{13}C$ [4]. A special application is non-destructive dating of wine based on the detection of $^{137}Cs$ (see this issue). An emerging dating technique related to geophysics is archaeo-magnetism that links the earth core dynamics at the origin of the geomagnetic field to objects made by firing through the magnetic properties of minerals (this issue).

The strategy of analysis depends on the questions to be answered, the nature of the materials, their alteration with time, the necessity of non-destructive analysis, etc. A large variety of materials is currently studied; metals, ceramics, stones, organic matter and their mixtures. Many techniques are used for the analysis of materials such as X-ray fluorescence (XRF), electron microscopy (SEM, TEM), X-ray diffraction (XRD), infra red absorption, etc. in the laboratory or at synchrotron radiation facilities. Accelerator based techniques have been used during the past 20 years at the C2RMF where ion beam analysis (IBA) has been turned into a routine tool for the study of art works,

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thanks to the development of an external microbeam allowing analyses at atmospheric pressure [5], thus avoiding the need to introduce the objects into a vacuum chamber. Our colleague Joseph Salomon played a key role in this achievement; no doubt that he would have participated in further applications (this issue) if illness had not robbed him from our research community in 2009.

Chemical element analysis is a common approach that it is based on the well established spectrometry of X-rays emitted under the impact of X-rays (XRF), of electrons in a scanning (SEM) or in a transmission (TEM) electron microscope, or of particles (Particle Induced X-ray Emission, PIXE) in an accelerator such as AGLAE (Accélérateur Grand Louvre d'Analyse Elémentaire located at the C2RMF) [5–8]. All the IBA techniques are available at AGLAE and are performed directly on objects giving information on the superficial layers (5–50 μm from the surface). PIXE is the most common because it gives quantitative compositions for concentrations as low as 5–10 ppm (impurity level). Since PIXE or XRF have limitations for light element analyses, AGLAE, using nuclei associated with $\gamma$-ray emission (Particle Induced Gamma Emission, PIGE) or nuclear reaction analysis (NRA), provides access to fluorine, boron, nitrogen, oxygen, etc. in art works. Depth profiling near the surface can also be obtained by IBA, for instance using resonant NRA [9]. Such profiling is usually performed at AGLAE by Rutherford back-scattering (RBS) [8]. Hydrogen profiling is also performed by elastic recoil detection analysis (ERDA) with $\alpha$-particles [9].

Synchrotron radiation methods find an increasing number of applications. Similar to AGLAE, intense radiation beams offer powerful techniques combining high spatial resolution, high sensitivity, and access to various physical and chemical information. There are various examples of applications, going from "hard matter", glass or metals, to "soft matter", such as paper, textile, wood and also *hybrid* materials, such as cosmetics or paintings. In cosmetics from ancient Egypt, lead compounds are ubiquitous, with mostly black lead sulphide (PbS) and white lead carbonate ($PbCO_3$) for eye make-up [10]. Unexpected white constituents (laurionite PbOHCl; phosgenite $Pb_2Cl_2CO_3$) have been identified by XRD; these compounds are not found in nature and have been synthesized in ancient Egypt by wet chemistry [10]. Laurionite and phosgenite were added because of their pharmaceutical properties.

Variable energy X-ray radiations are particularly suited for painting analyzes. Studies can be performed directly on the entire painting, for example, by K-edge imaging (radiography with X-rays of energy below and above the absorption edge), which will offer a direct visualization of the elemental distributions. Paintings exhibit multi-layered structures, with layer thicknesses of $\sim$10 μm, hence the interest of micro-imaging techniques. In addition, paintings are very complex in term of chemistry, as they are made of mineral and organic matter in the form of amorphous and crystalline phases. Accordingly, a multi-modal approach is essential to solve the chemical complexity of such *hybrid* materials. In particular, the combination of XRD, XRF, X-ray absorption near edge spectroscopy (XANES) and FTIR (infra red) spectroscopy is a key tool for the complete elucidation of painting compositions. The combination of a microscope with FTIR spectroscopy is a decisive step for such studies (this issue).

These composite materials are a challenge not only for the description of their structure and chemical composition at scales from 1 mm to 10 nm, but also for the identification of the mechanisms at the origin of their physical properties. Many of the applications require optimized mechanical properties such as strength or hardness. On the contrary, manufacturing includes a step of forming that is facilitated for soft materials. Examples of both aspects are given in this issue with the rheology of *hybrid* materials and the properties of wood used in constructions. The micro-structure may also be at the origin of the appearance of objects. For instance, ceramics have been covered with coloured glazes for thousands of years. In some cases, ceramics have a *lustre* shine which is due to copper and silver nano-particles distributed into a thin layer (100–200 nm thick) under the glaze surface. External beam RBS provides a fast and non-destructive technique to obtain concentration profiles of copper and silver in artworks [11]; it is currently performed on valuable *lustre* wares from museum collections [12]. The remarkable optical properties of such metal–glass composites are now well understood (this issue). Potters and glass-makers who developed the fabrication of these materials can be considered as early "nano-technologists". Nano-particles were also produced in the process of dyeing hair and wool black. Indeed, 5 nm size PbS grains are found in hair after applying a 2000 year old recipe with $PbO + Ca(OH)_2$ [13].

The appearance of artworks and objects from the cultural heritage is crucial, in particular their colour, gloss, touch, etc. It may result from the intention of the artist/craftsman or from alteration with time. Uncovering the history of these objects is performed with the help of various kinds of beams (particles, electromagnetic radiations from terahertz to $\gamma$-rays) allowing their multispectral non-destructive examination and analysis. Emerging techniques will soon allow making this in 3-dimension directly on works of art. It requires dedicated machines in laboratories close to the objects (this issue). Transportation to large scale facilities of valuable or oversize objects is a strong limitation for their study.

Portable light weight systems are an alternative and are available for Raman, XRF and XRD [14], infra red and Raman spectroscopy, etc. Finally, let us insist on the importance of close collaboration between specialists from many disciplines including physicists, chemists, etc. and curators, art historians, conservators, archaeologists, etc.

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