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Synchrotron X-ray for Archaeometry: state-of-the-art and future perspectives

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***Abstract* – X-rays techniques present several valuable advantages in the field of archaeometry. Using X-rays, structural and chemical details can be obtained through a non-destructive interaction. Synchrotron radiation sources offer x-ray beams of extraordinary intensities and energy tunability, resulting into unprecedented spatial resolution and enhanced elemental selectivity and chemical sensitivity. Archaometry, in its constant effort to interpret the past through the application of scientific techniques, has witnessed an extensive employment of synchrotron radiation. In addition, thanks to the advancements in X-ray production and optics design, and to the acquisition of higher-level technical and scientific expertise, synchrotron facilities have undergone a tremendous evolution in the last decades, approaching new scientific frontiers. In this work, we will present recent achievements that could be of interest for archaeometry. After the analysis of the present situation, we will delve into future perspectives. Scientific case studies will be thoroughly discussed as well as technical potentialities yet to be fully exploited.**

I. INTRODUCTION

Archaeometry, a multidisciplinary field at the intersection of archaeology, materials science, and physics, aims to uncover the secrets of ancient civilizations. This can be done through the analysis of a ancient artifacts by means of advanced analytical techniques [2]. In such field, dealing with samples that are one-of-a-kind is no extraordinary thing. Indeed, many artifacts are unique or available in limited numbers of pieces. This requires for a careful experimental design to avoid any damage to the precious samples.

Among the countless techniques available, X-ray-based analyses have shown a tremendous potential: given their non-destructiveness, their chemical sensitivity, and their elemental selectivity, x-ray beams are often a good choice when it comes to structural or chemical investigations of ancient findings [3, 4] In the wide X-ray sources panorama, synchrotrons have emerged as ground-breaking tools, revolutionizing the field and enabling unprecedented discoveries. In this work, we will explore the crucial role of synchrotron radiation in unraveling the mysteries of our past examining what has been done so far and what could be done in the future using the recent advances in synchrotron radiation methodologies.

II. DISCUSSION

Archaeometry exploits the scientific analysis of archaeological materials to gain insights into their composition, structure, and manufacturing processes. This kind of information is then interpreted on the basis of the historical context, to obtain details on ancient civilizations, shedding light on their technological advancements, craftsmanship, trade networks, and cultural practices. By combining traditional archaeological methods with cutting-edge scientific techniques, archaeometry provides a more comprehensive understanding of the past.

Synchrotron sources produce light from the IR to the hard X-ray range and have widely been used for archaeometry. Synchrotrons' highly focused and tunable beams are invaluable for investigating various properties of materials with unparalleled precision. Indeed, synchrotron radiation can probe the chemical and structural details of matter while preserving the integrity of the specimen [1]. Non-destructiveness stems, in fact, from the X-ray interaction with matter and it is not a prerogative of synchrotrons: the same is achieved by laboratory sources. Nevertheless, synchrotron radiation offers several advantages that are unattainable using laboratory sources.

The most striking assets of synchrotrons are the high flux and brightness of the beam. These represents obviously a great benefit, but many more could be added to the list [5]. Adjustable beam-sizes, and energy tunability, for instance, carry a huge potential as they allow to perform elemental analysis and/or chemical speciation from mm down to the nm range [6]. Combining these intrinsic benefits of synchrotrons, sensitive and accurate analyses of archaeological materials can be routinely performed, ensuring the detection and characterization of trace elements and compounds, even in small or complex samples, which may be challenging with conventional X-ray sources. In techniques such as X-ray fluorescence spectroscopy (XRF), high intensity and small beam size can be used to obtain an elemental mapping of the sample surface with a spatial resolution ranging from the mm to the nm scale, thus covering different lengthscales. Furthermore, exploiting the fine energy tunability, the identification of elements in archaeological materials can be carried out with remarkable precision, revealing valuable information about the composition, provenance, and trade networks of artifacts [6, 7, 8].

Regarding structural features, a useful resource is represented by X-ray diffraction (XRD): this technique can investigate structural parameters of crystalline materials. It can identify and quantify different crystalline phases and obtain detailed information on the average crystalline lattice probed by the incoming X-ray beam. This kind of information can be exploited, for instance, to shed light on the provenance of marble. In cases where other techniques fail, XRD can easily and with high degree of confidence distinguish among similar marbles having different origin. This was the case of Carrara marble discussed in a recent work [9].

A. *Energy Tunability*

The capability of selecting a particular energy can be beneficial for any technique, but for absorption-based analyses, it represents a real game changer. Photoemission, absorption, fluorescence emission all depend on the energy of the incident X-rays. The probability of interaction and, thus, the magnitude of the signal observed in the aforementioned cases, depends dramatically on the incident photon energy [5]. This stems directly from quantum mechanics and is the reason why absorption-based techniques are intrinsically characterised by an unprecedented chemical sensitivity. XRF spectrometry can provide a quite clear example of this. XRF spectra can be used to evaluate the chemical content of a sample and, in this respect, energy tunability plays a crucial role, as shown in Fig.1. The two spectra reported in the plot were recorded at the XRF beamline of Elettra [10] on the same sample (a high-purity gold coin), using two monochromatised SR-beams of different energy: 10 (black line) and 11.6 keV (red line). The two energies were selected using a Si(111) monochromator. The high energy beam, above the Pt L3 edge (11.564 keV), excites the fluorescence emission that gives rise to the peak around 9.5 keV in the red spectrum. Such peak is absent in the black spectrum due to the exciting energy being lower than the Pt L3 absorption edge. Here, thanks to the benefits offered by high energy-resolution and energy tunability, one can highlight the presence of elements even at very low concentrations.

Carrying out absorption-based techniques at a synchrotron means having the possibility of optimising the sensitivity to a particular element. In XRF measurements, energy tunability can be used to reconstruct lost images, providing striking examples of the capability of the technique [11]. Similar applications are represented by the analyses of ancient manuscripts, such as the Dead Sea Scrolls. XRF studies first revealed the elemental composition of the ink, providing insights into ink recipes and origins, and then unveiled hidden text and layers of parchment, aiding in deciphering damaged or overwritten texts [12, 13]. Also, energy tunability can be exploited to perform X-ray Absorption Spectroscopy (XAS). XAS is based on the measurement of the absorption coefficient over a certain energy range. The range is chosen near the absorption edge of one element of interest. From the analysis of the variation of the absorption coefficient, one can investigate the oxidation state of the element, and obtain information on different phases, including the quantification of each chemical species. Such information proves valuable when trying to identify the provenance of some soil (as in the case of Fe oxides in [8]), or to find remedy to degradation [14].

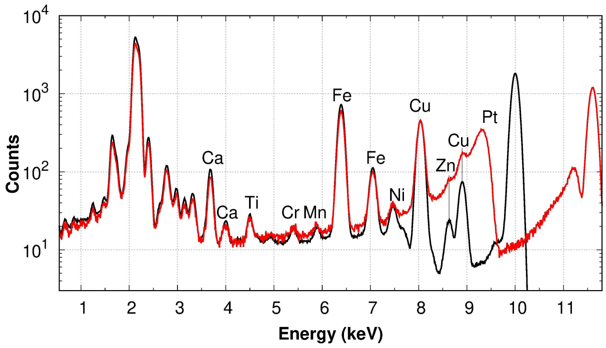

Fig. 1. Two XRF spectra collected on the same sample, with the same experimental parameters (sample-detector distance, dwell time) using two monochromatic beams of different energies: 10 keV (red line) and 11.6 keV (black line). The higher energy spectrum is showing a peak around 9.5 keV related to the Pt L emission which is absent in the lower energy spectrum. The sample, a high-purity gold coin, contains Pt as a trace element contaminant. The comparison of the two spectra demonstrate how the energy tunability is crucial to highlight the presence of certain elements even when their concentration is very low.

B. *Micro- and nano-analytical capabilities*

Synchrotron radiation techniques enable high-resolution imaging and analysis at the micro- and nano-scale. X-ray micro- and nano-beams can be used to investigate small regions of interest within artifacts, providing detailed information about local composition, structure, and/or degradation patterns.

All analytical techniques (including XRF, XAS, XRD, X-ray Photoemission Spectroscopy (XPS), imaging techniques, etc.) can benefit from a higher spatial resolution. Depending on the scientific question and on the nature of the sample, one can choose to focus on a particular length scale. Selecting a beam size of comparable dimension, the details of the sample can be studied using one or, more often, a set of complementary investigation tools.

In fact, a multi-modal approach enhances the understanding of archaeological materials by providing comprehensive data on elemental composition, mineralogical phases, chemical states, and structural information [17].

C. *The IR case*

Synchrotrons deliver electromagnetic radiation in a wide range of wavelengths, including the infrared (IR) region. IR photons share with x-rays the non-destructive nature and have already proven their potential in cultural heritage studies.

For instance, IR spectroscopy is employed to identify and characterize organic residues on ancient artifacts. By analyzing absorption bands in the IR spectrum, one can determine the molecular composition of residues such as oils, resins, and adhesives, or identify organic materials on surfaces that may be challenging with conventional IR spectroscopy. This turns out pretty useful when one is trying to understand the materials and methods used in the production of ancient artefacts like violins [12], or when characterising pigments and dyes used in ancient artworks and manuscripts. From the examination of the absorption bands and molecular vibrations in the IR spectrum, it is possible to identify specific pigments, differentiate between natural and synthetic dyes, and gain insights into ancient coloration techniques [13].

D. *Limitations: need for planning*

Beyond the appealing opportunities that synchrotrons offer, they do present some details to be handled with care. One of these is represented by the access to synchrotron facilities. For academic researchers, access to synchrotrons is granted only after the positive evaluation of proposals. Even in that case, each experiment has limited time and every measurement has to be carried out within the allocated time slot.

This means that each data acquisition has to be carefully designed and prepared, and that research teams have to follow the data collection and be ready to correct any deviations from the expected direction. Every foreseeable variable should be known and accounted for, and every unexpected observation should be readily acknowledged and dealt with. This demanding way of working does not allow for improvisation. And, if we plan to improve the cooperation among different backgrounds in archaeometry, we must plan well in advance.

From the perspective of the single experiment, this means trying to get the most out of each experimental run and take full advantage of the benefit offered by synchrotrons. For instance exploiting complementary information accessible through different techniques, elemental sensitivity, chemical speciation, structural details at different length scales [17, 18].

However, this strategy should be adopted by the community, rather than by the single research team. Indeed, synchrotron facilities are under constant evolution and this is the era of the fourth generation light sources. Being ready to use such sources means starting to grasp the main differences with the previous generation sources. The first step is to acknowledge the improvements and limitation of the new facilities, and start planning future experiments, generating new ideas.

III. FUTURE PERSPECTIVES

Fourth generation light sources are spreading, and synchrotron facilities are continuously improving their instrumentation and beamline capabilities. Nowadays, new and better science can be achieved using these sources. Higher fluxes, better coherence, and smaller beams are already allowing unprecedented details in spatially-resolved studies, as well as quick measurement times on huge areas. On top of that we are observing the development of more efficient detectors, higher-resolution imaging systems, and novel analytical techniques.

The technical upgrades alone can result into new applications of well known techniques. In a recent investigation on the analysis of metallic alloys, XRF was broguht to a new level. Using a double-dispersive setup (D^2-XRF), detection limits of ppb have been achieved with a relatively simple setup. such setup ensures high-energy resolution (13 eV at Cu Kα) with a relatively large energy range (1 keV). These features enable one to resolve Pt and Au L fluorescence lines, overcoming the typical limitation of standard XRF in numismatics [19].

Nevertheless, all these advancements would be vain without the synergy between scientists and archaeologists. As was extensively explained eslewere[20], showing that the interaction of two different worlds like science and history can be challenging but also that “without the genuine dialogue provided by good science in partnership with meaningful questions, little of value is achieved” [20].

In this work, we discuss the capabilities of synchrotron radiation techniques for archaeometry, describing the state-of-the-art of such methodologies. On the basis of the evolution driven by the current developments, we present several examples of the novelties offered to the field of archaeometry. These novelties can be exploited only through a fruitful interactions between scientists and archaeometrists. The successful collaboration between these two worlds will benefit archaeometry enabling archaeometrists to obtain richer and more precise data, by pushing the boundaries of what can be revealed about archaeological materials. Moreover, the needs of the archaeometry community will boots and drive the evolution of the synchrotron radiation sources.

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