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The Cultural Heritage Platform at Elettra

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***Abstract* – The use of synchrotron radiation for the analysis of samples of historical and artistic importance has been increasing over the past years, and experiments related to the study of our cultural heritage (CH) have been routinely performed at many beamlines of Elettra, the Italian synchrotron radiation facility. The laboratory now offers a platform dedicated to CH researchers in order to support both the proposal application phase and the different steps of the experiment, from sample preparation to data analysis.**

I. INTRODUCTION

The range of materials studied in the field of CH is very broad and includes inorganic materials such as metals, stone, glass, ceramics, and pigments, as well as organic-based materials such as wood, paper, leather and antrhropological samples [1]. Several areas of investigations are involved, between them the most important are: restoration and conservation; analysis of alteration and corrosion products; identification of materials and technologies used to produce arcaheological manufacts and artistic objects; study of human evolution. Synchrotron radiation offers a large portfolio of anaytical techniques and several advantages, such as the unique non-destructive capabilities of most analytical approaches and the possibility of using synergically more X-ray techniques in the same environment.

Elettra, located on the outskirts of Trieste, is the Italian 2.0 - 2.4 GeV third-generation synchrotron radiation facility, which has been serving the national and international scientific and industrial community since 1993 (figure 1). A full description of the facility can be found at ref. [2]. Due to the high amount of proposals in the field of CH, Elettra has recently created ECHO (Elettra Cultural Heritage Office), an equipe of scientists who assist CH researchers in order to support both the proposal application phase and the different steps of the experiment, from the sample preparation to the data analysis. The following paragraphs describe the beamlines involved in the project and some examples of applications.

Fig. 1. Aerial view of Elettra

II. MCX

The beamline Material Characterization by X-ray diffraction (MCX) is the general purpose powder diffraction beamline at the Elettra synchrotron source in Trieste, Italy, one of currently four diffraction beamlines at Elettra [3]. The beamline is designed to host a wide range of experiments, which cover many scientific fields with standard applications such as phase identification and structure determination using the Rietveld method or microstructure determination by line profile analysis. The standard experimental setup consists of a four-circle diffractometer equiped with receiving slits or an analyser crystal and a scintillator detector. As an alternative, a multi-channel analyser can be installed. This can be used to eliminate the background signal resulting from the fluorescence of the sample in a diffraction experiment. It also allows measuring X-ray fluorescence from the illuminated spot on the sample. This way chemical element analysis may be performed on the same spot where the diffraction is being measured.

The capabilities of the beamline can be illustrated by the characterization of alteration products on grisaille glass originating from large windows of the Basilica di San Giovanni e Paolo in Venice [4]. A large number of degradation products and original pigments could be identified, which allowed the proposition of a deterioration mechanism. A typical diffraction pattern is shown in Figure 2.

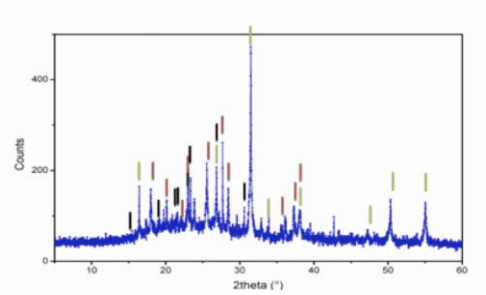

Fig. 2. Diffraction pattern of a part of the grisaille of fragment SSGP1. The positions of the diffraction peaks of the spinel $CoAl_2O_4$ (green), laurionite PbCl(OH) (black) and Anglesite $PbSO_4$ (red) are indicated.

Clearly, the signal to noise ratio is low with a large number of diffraction peaks.The maximum count rate obtained for this measurement was ~400 counts per second. This is a clear indication that the amount of crystalline material is very small and that, therefore, it is necessary to use synchrotron radiation to study these fragments in order to get some information out of the data. The peaks in the diffraction pattern of the grisaille part of a fragment were confronted with the patterns in the PDF4 database. Most of the peaks could be attributed to the spinel $CoAl_2O_4$, to Laurionite (PbCl(OH)) and Anglesite ($PbSO_4$).

III. IUVS

The synchrotron-based UV resonant Raman scattering facility implemented at IUVS beamline@Elettra [5] has been demonstrated to be a valid tool for addressing a large array of open problems in the field of CH, allowing to overcome the most critical limitations in the application of conventional Raman spectroscopy to the analytical characterization of art materials. The advantages offered by UV Resonant Raman technique (UVRR) concern i) the improvement of signal-to-noise ratio of Raman bands excited by using wavelengths in the UV range, ii) the strong quenching in the Raman spectra of the fluorescence emission backgrounds (arising also from specimen degradation and presence of impurities) that in many cases constitute a serious limitation in the acquisition and analysis of Raman spectra of historical-artistic materials and iii) the selective enhancement of the Raman bands associated to specific functional groups by exploiting the resonance conditions occurring at different excitation wavelengths in the UV-range (see figure 3).

The unique tunability provided by the synchrotron radiation source gives the possibility to a selective choice of the excitation energy that it is possible to match with the experimental conditions, allowing to overcome the limitation of conventional UV laser sources at fixed energy of emission. Additionally, the experimental layout available on IUVS offers the opportunity to choice two different sampling modalities, by carrying out macro- or micro- UVRR measurements, in order to select the best experimental conditions depending on the type of sample under investigation.

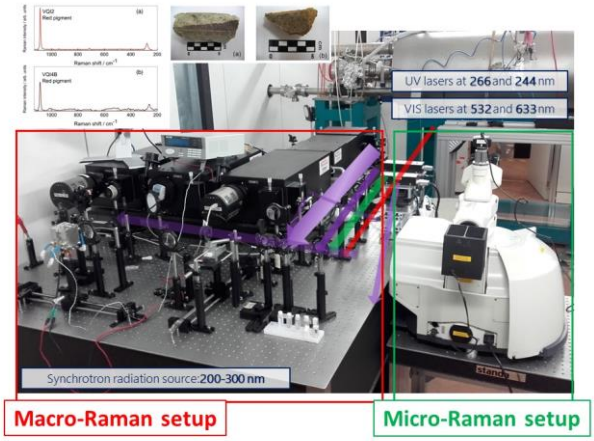

Fig. 3. experimental setup for macro- and micro- UV Resonant Raman spectroscopy measurements at IUVS. The exciting radiation source is provided by synchrotron radiation and by conventional laser sources in the UV and visible range.

The potentialities of UVRR technique in the analytical investigation of materials related to the field of CH have been recently corroborated by the results obtained in the spectroscopic investigation of Roman decorated plasters arising from *Villa dei Quintili* and in the analysis of TiO2-based nanostructured coatings for preventing biological degradation on stone surfaces [6].

IV. ESCA MICROSCOPY

The Scanning photoelectron microscope (SPEM) hosted at the ESCAmicroscopy beamline [7] allows to combine chemically surface sensitive measurements with high spatial resolution. The experimental apparatus allows to carry out a manifold of experiments, aiming at quantitative and qualitative chemical characterisation of morphologically complex materials. The SPEM uses a Fresnel-based optics to demagnify the synchrotron X-ray beam down to a submicron spot (130 nm of diameter). There are two operation modes: 1) acquiring ESCA spectra from a submicron spot on specific points on the samples surface with energy sensitivity within 180 meV, and 2) scanning the samples to highlight the spatial distribution of the different elements and chemical species (chemical maps), with an effective spatial resolution down to 80-100nm.

As an example, we show results obtained in the characterization of a late Bronze Age artefact (ca. 1100 BCE) exposed to a coastal environment [8]. The investigated object consists of a segregated cast bronze. The prevailing corrosion form is preferential attack of Sn-rich phases, accompanied by a synergistic type of Sn and Cu attack triggered by the peculiar type of decuprification

taking place in a bronze disease framework and characterized by the formation of Sn(OH)Cl as a result of local HCl generation in the Cu corrosion process.

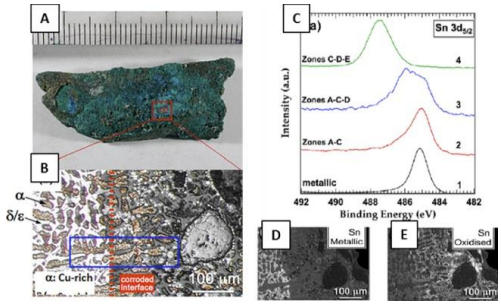

Fig. 4. (A) and (B) optical image. (C) ESCA spectra in different points. (D) and (E) chemical maps at metallic and oxided tin of the same region showed in (B)

In particular, the SPEM capability in the morphochemical investigation of samples is shown in figure 4.
These results have allowed to develop and implement at the practical conservation level a novel electrochemical approach, based on ionic liquid, for the definitive remediation of items affected by bronze disease. Specifically this technique allows the penetration of the electric field into the deep, screened pits present on the surface, affecting both reduction of copper and extraction of chloride ions.

V. XAFS

X-ray absorption spectroscopy (XAS) provides chemically specific short range structural around the photoabsorber atom. Together with x-ray diffraction (XRD) that, on the other side, is sensitive at a longer range, XAS allows a full structural characterization of materials. For this reason several efforts have been made to develop experimental set-ups allowing the combined collection of XRD and XAS for different applications using both energy dispersive and energy-scanning configurations. The XAFS beamline XFS is installed on a bending magnet source and it has been opened to users since 2004. It was designed to cover a wide energy range: from 2.4 to 27 keV meeting the needs of a large number of researchers in the area of conventional x-ray absorption spectroscopy. For this reason the research activity at the XAFS beamline at ELETTRA is quite diverse and ranges from catalysis to material and environmental science [9].
In a recent work, two lustred majolica shards, from Hispano-Moorish and Italian productions, were studied in two different regions (the blue pigment and on the lustre), with the aim to achieve a better understanding of the technological processes and materials used in different productions [10]. On the blue pigment, XAS spectra were measured at the Co, Ni and Cu K-edge. Concerning the Co, for both productions the XANES spectra pointed out the poor crystallinity of the Co environment as well as a main contribution of Co^{2+} ions at tetrahedral sites.

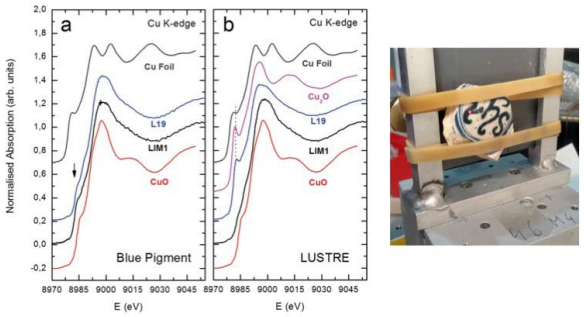

Fig. 5. Cu K-edge XANES spectra of CuO, Cu2O, metallic Cu foil and of the samples on the blue pigment (a) and on the lustre (b).

Ni is present as NiO but some differences arise between the two samples. In fact, despite the sample being amorphous, as expected, in the Hispano-Moorish sample the NiO structure is ordered up to the second coordination shell (Ni–O–Ni). The Cu spectra in the blue parts are quite similar, and indicate that Cu is close to Cu^{2+}, even though it is possible to observe, for both samples, an edge modification that suggests a started reduction of the Cu ions (figure 5).

VI. SISSI

SISSI, Synchrotron Infrared Source for Spectroscopy and Imaging, is the infrared beamline at Elettra [11]. It extracts SR beam from visible to THz, allowing to exploit the flux and brightness advantage of IRSR for a large variety of experiments. The Chemical and Life Sciences branch of SISSI is equipped with state-of-the-art Fourier Transform InfraRed (FTIR) interferometer and Vis-IR microscope, that grant the possibility of spectroscopy experiments over the entire IR regime and FTIR microscopy and imaging in the Mid-IR. The beamline versatility, the possibility to perform experiments under environmental conditions, the minimal sample preparation, the non damaging nature of IR light and the superior spectral quality provided by IRSR make SISSI an ideal tool for CH research. Organic and metalorganic constituents of ancient and modern artifacts, such as pigments, binders, can be investigated for shedding light of the ancient painting techniques and possible degradation pathways.
As an example, imaging of metal oxalates/ carboxylates in the paint layers of extensively deteriorated post-Byzantine murals was done (figure 6), for investigating their possible association with the ageing of organic substances used as binding media in the original painting [12]. Prehistoric samples have been also recently analyzed, in order to identify the chemical nature of very

minute starch fragments on ground stones dating back 40,000 years or fiber-like residues preserved within one of the anthropogenic cut marks on the eagle talons and modified by Neandertals some 130,000 years before present.

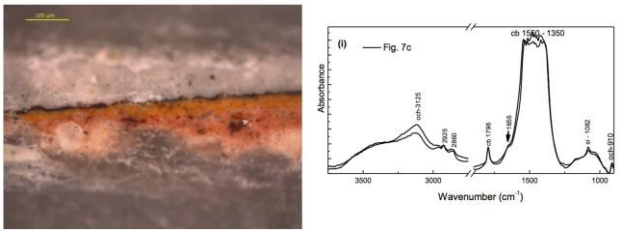

Fig. 6 - Visible image of a cross section of a fragment consisting of an upper white layer and two bellow brown and orange paint layers, as well as a preparation layer; FTIR spectrum at 1655 cm^{-1}. The main vibrational bands of yellow ochre (och), $CaCO_3$ (cb), and the silicate (si) band are indicated.

VII. SYRMEP

X-ray microtomography is a powerful imaging technique used to characterize material microstructure in three dimensions, with resolution of the order of microns or below, in a nondestructive way and without requiring a specific sample preparation. The X-ray μ-CT investigations at ELETTRA are carried out using the SYRMEP beamline, which provides a laminar monochromatic X-ray beam in the energy range between 8.5 keV and 35 keV [13]. Furthermore, phase-sensitive imaging techniques using highly coherent, hard X-rays from third-generation synchrotron sources have the additional advantage to allow imaging of samples with very low absorption contrast, such as light-element glues and consolidants.

Thanks to the combined approach of synchrotron radiation phase-contrast tomography, and the use of large detectors coupled with laminar X-ray beams, SYRMEP demonstrated the advantages of non-invasive three-dimensional analysis of ancient musical instruments. In figure 7, a cross section slice of a 1757 Guadagnini violin clearly shows that the bass bar had been removed and glued on a patch, while two additional patches appear on the right part of the top plate. An accurate measurement of the wood thickness can be performed in every part of this cross section, and the tree rings can be measured for dendrochronological applications [14].

Another powerful instrument for CH at ELETTRA is TomoLab, a cone-beam micro-CT system, equipped with a microfocus X-ray tube, with a minimum focal spot size of 5 μm, in a voltage range from 40 to 130 kV, and a maximum current of 300 μA. Thanks to its configuration, also at TomoLab it is possible to perform phase-contrast microCT measurements [15].

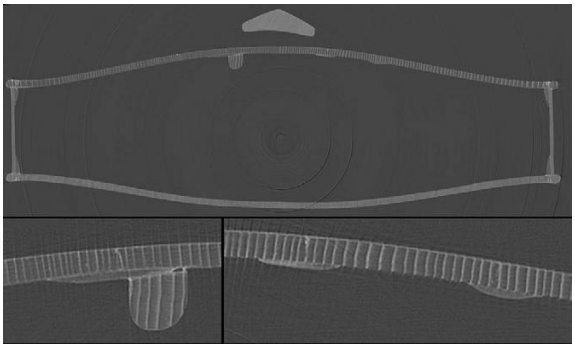

Fig. 7. Tomographic slice of a 1757 Guadagnini violin at the tailpiece level. The left inset shows the bass bar glued on a patch, while the right inset shows two additional patches on the top plate.

VIII. TWINMIC

TwinMic, the European Soft X-ray Transmission and Emission Microscope, integrates the advantages of complementary scanning and full-field imaging modes into a single instrument, operating in the 400-2200 eV energy range. The spectromicroscopy experimental station combines scanning and full-field imaging in a single instrument, with contrast modes such as absorption, differential phase, interference and darkfield (figure 8).

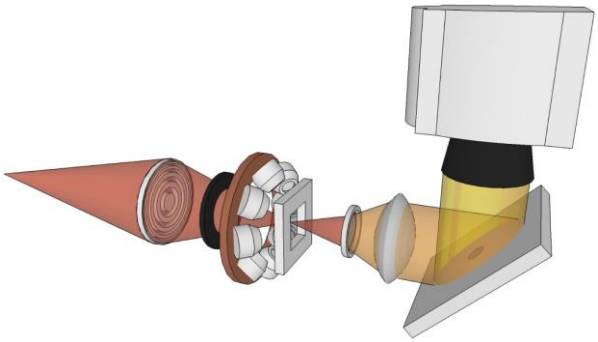

Fig. 8. Scheme of the TwinMic final stage. On the left a zone plate forms a microprobe which is sent to the specimen on a scanning stage for XRF analysis. On the right a configured transmission detector system with visible light converter.

Typically, scanning transmission X-ray microscopy images are simultaneously collected in transmission and differential phase contrast and can be complemented by chemical and elemental analysis using across-absorption-edge imaging, X-ray absorption near-edge structure or low-energy X-ray fluorescence. The lateral resolutions depend on the particular imaging and contrast mode chosen [16].

This combination opens unique possibilities for the investigation of material growth and degradation, with

obvious applications in the restoration and conservation of ancient metal manufacts. Using a specially developed vacuum-tight electrochemical liquid cell, it was possible to perform static and dynamic in situ characterization of the mesoscopic Ag corrosion and deposition morphology at sub-micron level. Corrosion and electrodeposition morphologies typical of different model-systems were considered, and, time-dependent anodic and cathodic morphology evolution types were recorded [17].

Fig. 9. The XRF monochromator

IX. X-RAY FLUORESCENCE

X-Ray Fluorescence is a highly versatile beamline working in an energy range between 2 and 14 keV (figure 9). The beamline is optically designed to present beam parameters needed for high level measurements in spectroscopy as well as in microscopy [18]. The beamline hosts a ultra-high vacuum chamber, operated in partnership with the IAEA [19]. Thanks to the combination of a tuneable monochromatic beam and of a flexible 7-axis manipulator of the UHVC end-station, synergistic application of various X-Ray Spectrometry and Spectroscopic Techniques are enabled. Elemental analysis for inhomogeneous samples (XRF), for trace analysis (Total Reflection XRF) or for depth resolution in the nanometer range, chemical speciation of specific elements (XANES) become feasible within the same instrument.

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