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The ID21 X-ray and infrared microscopy beamline at the ESRF: status and recent applications to artistic materials

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The ID21 beamline (European Synchrotron Radiation facility, France) is a multi micro-analytical platform combining X-ray and infrared micro-probes, for characterization of elements, species, molecular groups and crystalline structures in complex materials. Applications are mainly in the fields of cultural heritage, life science, environmental and earth sciences, materials sciences. Here, we first present the status of instruments: (i) the scanning micro-spectroscopy end-station, operating from 2.0 to 9.2 keV, under vacuum and offering cryo conditions, for the acquisition of 2D micro X-ray fluorescence (µXRF) maps, single point micro X-ray Absorption Near Edge Structure (µXANES) spectra and speciation maps with sub-micrometric resolution; (ii) the XANES full-field end-station, operating in the same vacuum and energy conditions, for the acquisition of hyper-spectral radiographs of thin concentrated samples, resulting in speciation maps with micrometric resolution and millimetric field of view; (iii) the scanning micro-X-ray diffraction (µXRD)/µXRF end-station, operating at 8.5 keV, in air, for the acquisition of 2D crystalline phase maps, with micrometric resolution; and (iv) the scanning infrared microscope, operating in the mid-infrared range for the acquisition of molecular maps and some structural maps with micrometric resolution. Recent hardware and software developments are presented, as well as new protocols for improved sample preparation of thin sections. Secondly, a review of recent applications for the study of cultural heritage is presented, illustrated by various examples: determination of the origin of the color in blue Chinese porcelains and in brown Sèvres porcelains; detection of lead in ink on Herculaneum papyri; identification and degradation of modeling materials used by Auguste Rodin and of chrome yellow pigments used by Vincent van Gogh. Cryo capabilities are illustrated by the analysis of plants exposed to chromate solutions. These examples show the variety of materials analyzed, of questions tackled, and particularly the multiple advantages of the ID21 analytical platform for the analysis of ancient and artistic materials.

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1. Introduction

The project to build an X-ray microscopy beamline at the European Synchrotron Radiation Facility (ESRF) was originally proposed in 1992. The beamline construction started in June 1996 and the first radiation tests were carried out in October 1996. One year later, in September 1997, the beamline welcomed its first external users. In its original design, ID21 was dedicated to X-ray imaging and spectro-microscopy in the 0.2-7 keV energy range with two independent end-stations on separate branchlines: a scanning X-ray microscope (SXM) on the direct branch and a full-field imaging transmission X-ray microscope (TXM) on the side-branch.1 Driven by both a strong demand from users for specific techniques and a more science-oriented in-house research activity, the ID21 activities slightly diverged from the original plans. In particular, the full-field X-ray imaging branch and X-ray microscopy at very low energy (water window) were phased out. On the contrary, all the developments related to scanning X-ray microscopy were boosted with emphasis on micro X-ray Absorption Near Edge Structure (µXANES) Spectroscopy and micro X-ray fluorescence (µXRF) in the 2-7 keV range (in particular at sulphur and iron K-edges).² A major reorientation, decided in 2002 and implemented in 2003-2004, was the construction of a complementary Fourier-transform infrared (FTIR) end-station at ID21.3 In 2007/2008, the SXM benefited from a major refurbishment, with fundamental improvements of focusing optics, detectors, sample stage and environment in particular for cryo-microscopy, as well as control thanks to a user friendly graphical interface.⁴ In 2008–2010, an additional end-station was developed and installed downstream of the SXM for so called "Full-field XANES" experiments.5 More recently, the side-branch has been completely refurbished to accommodate a new end-station dedicated to powder-like micro X-ray diffraction (µXRD) combined with µXRF, in 2D scanning mode, further complementing the set of 2D micro-analytical techniques available at the ID21 beamline. The first part of the present paper details the current status of these different end-stations.

The general scientific case of ID21 is the identification and localisation of unknown components in complex mixtures with sub-micrometric resolution and millimetric field of view. In terms of applications, the main user communities are from the fields of biology, environmental sciences and cultural heritage, each representing about 25% of beamtime. Beyond the context of ID21, synchrotron radiation (SR)-based techniques are increasingly used to analyse cultural heritage materials.⁶⁻⁹ As shown in the examples below and in Table 1, the ID21 X-ray and infrared microscopes can be applied to study almost all kinds of artistic materials, such as paintings, ceramics, glasses, plastics, wood and papyrus. Whatever the technical and methodological approaches, questions commonly tackled can be divided into two main categories: those searching for a better understanding of the past and those aimed at providing an educated projection of the future. More precisely, the analysis of ancient and artistic materials can reveal clues about the manufacturing processes developed over time and cultures and consequently about

possible exchanges between civilisations. They can also shed light on degradation mechanisms and can ultimately help optimize strategies for the preservation and conservation of cultural heritage objects. The heterogeneity of the samples from the object scale (>m in some cases) to the sub-micrometric scale requires the application of both portable imaging instruments for large scale (usually on-site) analyses on entire objects and nano-probes for off-site characterization of tiny fragments. For ex situ studies, synchrotron radiation is exploited to get insights into the chemical or/and structural compositions of samples. The complexity of the materials (inorganic + organic, crystallized + amorphous, major to trace) requires the combination of several complementary analytical techniques (to probe elements, metallic species, organic molecular groups and crystalline structures) performed in imaging mode with sub-micrometric resolution, to reveal the relative localisation and interdependence of the different compounds. The rarity and limited size of fragments (when available) make the use of non-invasive methods preferable, hence the success of methods based on light-matter interactions.

Over the last 10 years, the ID21 beamline has welcomed many experiments focusing on the study of ancient and artistic materials. This popularity can be explained by the very good agreement between the technical requirements associated with the study of artistic materials (complexity and heterogeneity at the micron scale) and the instrumental capabilities offered at the beamline. The second part of this paper reviews various recent applications of the ID21 instruments in the field of cultural heritage.

2. ID21 beamline, ESRF: present status

The ESRF is a high energy electron accelerator with an electron energy of 6.02 GeV, maximum intensity of 200 mA and emittance of $\varepsilon_{\rm h} = 4$ nm (horizontal) and $\varepsilon_{\rm v} = 4$ pm (vertical). The ID21 beamline presently hosts four complementary end-stations (Fig. 1). Notably, the X-ray platform is composed of two branches: the direct branch allocates (i) a scanning X-ray micro-spectroscopy end-station and (ii) a full-field spectroscopy end-station, while the side-branch hosts (iii) a scanning X-ray microscope dedicated to μ XRD mapping. Furthermore, (iv) a scanning synchrotron infrared microscope, that is independent from the X-ray source, is also available.

2.1. The X-ray source and primary optics

The three X-ray instruments have in common the X-ray source and the primary mirror system. The X-ray source is a 4.8 m long low-beta straight section and is equipped with three 1.6 m long undulators: two with a 42 mm period (U42) and one with a 32 mm period (U32). They can be scanned continuously during X-ray Absorption Spectroscopy (XAS) acquisitions and two undulators can be used simultaneously for experiments requiring high flux. The U42 elements deliver maximum X-ray intensity in the energy range 2–6 keV while the U32 device is used to cover the energy range 6–9.2 keV.

				Information provided by			
Materials	Typical problematics	Typical samples	Sample preparation	μXRF	XANES ^{8,9}	μXRD	μFTIR
Ceramics: analyses can be done on the different parts: body, glaze, pigments	Establishing relationship between colour and composition; rediscovering historical manufacturing processes	Fragments from historical material; model samples prepared under various firing conditions	Prepared as cross- sections or ideally as thin sections for transmission analyses	Elemental maps can reveal specific diffusion of some elements (<i>e.g.</i> from pigment particles) during firing ^{40,42} (cf . Fig. 5 and 6)	Identification and 2D localisation of element speciation in glaze and in pigment particles; at ID21: $^{40.42}$ at ID21 and at beamline 6-2c, SSRL: 23,24 (<i>cf.</i> Fig. 5 and 6)	Structural identification of pigments in particular determination lattice parameters. Can be related to firing conditions and ingredients murity ⁴⁰ (<i>cf</i> Fiv. 5)	
		Pure ingredients	Powders		Macro XANES to establish a relationship between colour (<i>e.g.</i> visible spectroscopy) and element chemical environment ⁴¹ (cf . Fig. 6)	G - G - F	
Glasses: analyses can be done on the different parts: glass matrix, crystals; stained degraded areas	Establishing relationship between colour and composition; rediscovering historical manufacturing processes. Understanding degradation processes and evaluating conservation	Fragments from historical material; model samples	Prepared as cross- sections	Elemental maps to assess specific diffusion of some elements $(e.g.$ leaching ³⁵)	Determination of Sb speciation in matrix and crystals in opaque glasses ¹²⁻¹⁵ identification and localisation of degradation products (<i>e.g.</i> Mn bodies) and assessment of cleaning treatments ⁶⁸		Modification of Si-O in corroded glasses ³⁵
Paints: ⁶ analyses can be done on the different parts: support, ground layers, paint layers, varnish layers, restoration layers	treatments Establishing relationship between colour and composition; rediscovering historical manufacturing processes. Understanding degradation processes (factors and products)	Fragments from historical material; model samples artificially aged	Usually as cross- section but thin sections should be preferred ³⁶⁻³⁸	Elemental identification and localisation of pigments, fillers, degradation products, exogenous elements (e.g. pollutants) ³⁹	Identification and localisation of the speciation of elements from pigments and pollutants in unaltered and altered regions; ^{19,28,48-55,57-61} at ID21, P06 (Petra-III) and XFM (AS); ²⁰⁰ at ID21 and BL 2–3 at SSRL ⁵⁶ (cf ; Fig. 8)	Phase identification of original ingredients (pigments, driers) and alteration products, ²⁸ at BM16 (ESRF), ³⁹ at ID13 (ESRF), ³³ at ID13F (ESRF), ³⁴ at ID13F (ESRF), ³⁵ a	Identification and localisation of: binders, ^{29,36} pigments and fillers (<i>e.g.</i> hydroxy/ carbonates, sulphates), ³⁰ products of interaction of binders with pigments and driers, ^{28,53} restoration treatments, ²⁵ degradation products <i>e.g.</i> oxalates ^{31,50}

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Table 1 Overview of recent applications of ID21 instruments (possibly in combination with other beamlines) in the field of cultural heritage

Table 1 (Contd.)							
				Information provided by			
Materials	Typical problematics	Typical samples	Sample preparation	μXRF	XANES ^{8,9}	μXRD	μFTIR
Sculpture and design modern materials	Composition and degradation of plastics in design objects ³³	Fragments from historical material; model samples artificially aged	Thin sections				Identification and localisation of constitutive ingredients (ABS, proteins) and of photo-degradation products
	Composition and degradation of modern modelling materials	Fragments from sculptures	Cross-sections and raw fragments,	Assessment of elemental diffusion in demodation areas (of	Speciation of sulphur in unaltered and	Phase identification in crystallized	Identification and localisation of
	nouening materiaus (<i>e.g.</i> in Rodin's sculptures ⁴⁷)		pressed between diamond windows	uegraduoli areas (g. Fig. 10)	uegradation products	products	ingredients (morganic, organic and hybrid) in unaltered and altered regions (cf. Fig. 10)
Manuscripts	Identification of metals in ink on Herculaneum papyri	Fragment of papyrus	No preparation (surface analyses)	2D macro XRF maps to identify elements present in ink. 2D micro XRF maps to assess co-localisation of elements ^{44,45} (cf. Fig. 7)	(Tentative) identification of species present in ink (ID21 and BM26A) ⁴⁵	Identification phases present in ink and papyri, at ID11 (ESRF) ⁴⁴	
Miscellaneous	Identification of ritual blood in patina of Dogon-Tellem statuary ⁶⁹	Fragments from historical material	Cross-sections		Identification and localisation of Fe species (inorganic and in heme environment)		Identification and localisation of proteins
	Composition of varnishes of historical musical instruments ³²	Fragments from historical material	Thin section, if possible without embedding			Identification pigments, fillers, at BM02 (ESRF)	Identification and localisation of binders, pigments, fillers

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Fig. 1 Schematic layout of the ID21 beamline (top-view), with the different hutches, rooms, end-stations and main optical components. Elements installed at the construction of the beamline but which are no longer used are not represented. Distances given refer to source – first optics distances.

At 28 m from the source, a fixed-exit horizontally deflecting primary Si mirror system allows the rejection of high harmonics (attenuation by a factor $\geq 10^3$). Three coatings are available: Si, Ni and Rh, to cover the full energy range accessible at ID21. Most of the time (in particular for spectroscopy analyses) the coating is chosen such that only one harmonic (the fundamental) is reflected by the system. However, in particular for mapping simultaneously low Z (*e.g.* P, S, Cl) or heavy elements such as Pb using M series emission and high Z elements (*e.g.* Cr, Mn, Fe) with a balanced excitation, a double beam set-up can be used (selecting both first and third harmonics). A refurbishment of this mirror system is currently in progress.

At 35 m from the source, a multi-layer (ML, 200 layers of W/B_4C deposited on a Si substrate) can be inserted to steer the beam to the side-branch. The angle of incidence and corresponding reflected energy are 2.15° and 8.53 keV, respectively. The spectral width is 0.9% (corresponding to 77 eV).

Without deflection by this multi-layer, the incident beam goes to the direct branch, and its energy is selected by a fixedexit double crystal monochromator (Kohzu Precision Co., Ltd, Japan), cooled with a N₂ gas flow. Crystal pairs of Si(111) ($\Delta E/E = \sim 2 \times 10^{-4}$) or Si(220) ($\Delta E/E = \sim 9 \times 10^{-5}$) are routinely used for XAS experiments. During such acquisitions, the monochromator angle and the undulator gap(s) are synchronized for continuous scans. A Ni/B₄C multi-layer is also available ($\Delta E/E = \sim 1\%$) for flux-demanding non-spectroscopy experiments.

2.2. The scanning X-ray micro-spectroscopy end-station

The SXM operates in the 2.0–9.2 keV energy range, under vacuum (Fig. 2).⁴ In its standard use, the ID21 SXM offers 2D μ XRF for elemental mapping, and single point μ XANES for local speciation analysis. The beam can be focused down to ~0.3 μ m (ver.) \times 0.7 μ m (hor.), with a flux of 10⁹ to 10¹¹ ph s⁻¹ by means of a Kirkpatrick–Baez mirror system. A smaller beam spot can be obtained with zone plates ("ZP") at the expense of flux and beam stability during XAS scans. Macro-characterization of mm–cm samples can be easily performed with large beams (from ~300 μ m down to ~50 μ m), by employing slits or pinholes, without focusing optics. As seen in the example of



Fig. 2 Schematic top view of the scanning X-ray microscope and XANES full-field end-stations at ID21. Scales are not real. Volumes in light grey represent vacuum chambers.

Herculaneum papyri presented below (see paragraph 3.1.2) this offers the possibility of a hierarchical imaging of the matter. Samples are mounted in a vertical plan, oriented with an angle of 62° with respect to the incident beam. Samples are positioned and raster scanned using stepper motor (2 cm range, 1 µm resolution) and piezoelectric actuated (100 µm range, 10 nm resolution) translation stages. Various detectors are continuously mounted in the vacuum chamber to measure the incident beam intensity ("iodet"), the transmitted beam intensity ("idet") and the XRF emission. XRF detection mainly uses a large area (80 mm² collimated active area) silicon drift diode (Bruker, Germany). Alternatively, when the element of interest is highly concentrated, XANES can be acquired with a photodiode collecting all emitted (XRF and scattered) X-ray signals without energy discrimination. Finally, an in-house developed compact wavelength dispersive spectrometer gives access to an energy resolution of a few tens of eV,10 which was successfully used for the XAS analysis of different historical opaque glasses.¹¹⁻¹⁵ Samples are mounted into the SXM using a transfer chamber and a transfer cane. This allows the main SXM chamber to be kept under vacuum (10^{-4} mbar) during sample exchange.

Regarding sample environment, a vibration-free cryogenic stage is available for performing cryo-microscopy at 130 K.⁴ This cryogenic stage is a main request for users in biology and environmental sciences; it plays a fundamental role preserving the morphological structure of the sample and limiting radiation damage in sensitive samples such as plant or human tissues. In order to facilitate user experiments under cryoconditions, key auxiliary equipments were recently implemented: a glove-box for manipulation of samples and transfer to the sample holder in LN₂ and under inert atmosphere (N₂), a 70 L cryo-Dewar for temporal storage of cryogenic samples at 100 K, a canister gas phase cryo-Dewar that can be lend to users to transport samples from their institute to ESRF and a cryo-microtome that allows sectioning of samples on-site ensuring fast and efficient sample transfer of freshly cut samples into the SXM. A new version of the cryogenic stage has been recently commissioned where particular attention has been paid in optimizing the contact geometry of the sample holder and cold trap, and the sample fixation mechanism on the holder (for compatibility with Ultralene films, copper grids, and Si₃N₄ windows).

Regarding software, many efforts have been made and are in progress to improve data-acquisition, data-processing and dataanalysis. All microscope alignments and data acquisitions are driven through a fully integrated graphical user interface which includes on-line visualization of the sample through a videomicroscope and the possibility to grab sets of points or regions of interest from the visible image, as well as from previously recorded µXRF maps. Acquisition sequences can be easily and automatically generated from such sets of points, to perform the same measurement (e.g. XANES scans) over many sample positions. As an alternative to these multi-point XANES acquisitions, other macros were developed to acquire tens or hundreds of µXRF maps, at different energies, over the XANES energy range of the element of interest (XANES hyper-spectral mapping). The initial purpose was to develop a tool for µXANES of nano-objects and deal with the problem of beam drift $(\sim 1 \ \mu m)$ during XANES scans. In this hyper-spectral mapping approach, the beam drift can be precisely determined at each energy on the µXRF maps of an element fluorescing below the XRF signal of the element of interest. These µXRF elemental maps are not affected by the varying energy of incident beam



Fig. 3 Illustration of the "Spectrocrunch" package for hyperspectral map fitting, normalization and alignment on the analysis of chrome yellow alteration in Van Gogh paintings. (A) Visible light picture of a paint fragment from Falling Leaves (Les Alyscamps) (Arles, 1888; Kröller-Müller Museum, Otterlo, NL) embedded in resin and polished. The surface of the yellow paint layer is covered with a coating brown translucent layer. The white rectangle represents the area where the μ XRF maps shown in (C–F) and (I) were collected. (B) Cr K-edge XANES spectra of PbCrO₄ (red) and Cr(OH)₃ (green) and inset on the pre-edge peak region. The dotted line highlights the position of the Cr(vi) pre-edge peak (5.993 keV). (C and D) Cr and (E and F) Ba μ XRF maps recorded from the area shown in (A) at *E* = 5.993 keV (red) and *E* = 6.086 keV (green), (C–E) before and (D–F) after image realignment [map size (hor. × ver.): 49.7 × 16.25 μ m²; beam and step size (hor. × ver.): 0.7 × 0.25 μ m²]. Maps were normalized, dead-time corrected and fitted. (G and H) Cr XRF intensity obtained over the vertical profile shown by a blue arrow in (C) and (D). (I) Composite RGB distribution maps of Cr(vi) (red), Cr(iii) (green) and K (blue). (J) Result of the linear combination fitting (blue) of PbCrO₄ (red) and KCr(SO₄)₂·12H₂O (green) to the μ XANES spectrum (black) obtained from the particle indicated by a white circle in (I) (see^{19,20} for further details).

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(speciation independent) and are used to monitor the beam drift. The principle of this procedure is illustrated in Fig. 3. It shows speciation maps of Cr in lead chromate pigments in a painting fragment obtained from Falling Leaves (Les Alyscamps), by Van Gogh (Kröller-Müller Museum, Otterlo, NL). In particular, the analysis aims at determining Cr speciation at the paint/varnish interface (see below paragraph 3.2.2 for more scientific details). A 2D region was selected by including both the yellow paint layer and the superficial brown coating (Fig. 3A). The same μ XRF map was acquired twice: at E =5.993 keV [corresponding to the pre-edge peak position in the Cr K-edge XANES region profile, very intense for CrVI species (chromate anions), and almost absent for reduced chromium, cf. Fig. 3B] and at 6.086 keV [in the post-edge region, where all Cr species absorb equally]. Fig. 3C shows the two different energies Cr maps before image alignment (red, E = 5.993 keV; green, E = 6.086 keV). The main information is the presence of $\sim 2 \mu m$ diameter Cr(m)-rich particles in the coating (green colour), and the detection of mainly Cr(vi) species in the most internal part of the yellow paint (yellow colour). Additionally, the Cr distribution map suggests a very thin (\sim <0.5 µm) layer of reduced Cr at the paint/coating interface (see profile in Fig. 3G). To determine the beam drift between the two energies, we use the elemental map of another element showing a contrasted distribution. In this case, a slight beam shift of about one pixel both in the vertical and in the horizontal directions (pixel sizes (vert. \times hor.): 0.25 \times 0.7 μ m²) was deduced from the Ba maps (Fig. 3E). All the elemental maps, including those of Cr and Ba, can then be corrected for this shift (Fig. 3D and F). As a result, it can be seen that the very thin superficial layer of reduced Cr was indeed an artefact of the beam drift, and is not observed after realignment (Fig. 3H). The so-called "Spectrocrunch" python software library includes all the routines needed for this data processing: dead-time correction, normalization by i_odet signal (proportional to the incoming flux), fitting using PyMca software (taking the different primary beam energy for each map into account)16 and image realignment based on feature detection¹⁷ or optimization of mutual information between maps.18 In the present example, just two energies were sufficient to obtain qualitative speciation maps, however the software can be similarly used to fit and align maps at hundreds of different energies, allowing extraction of whole XANES spectra.

 μ XANES point analysis at the Cr K-edge gives insights into the nature of the Cr(m)/K-rich particles (Fig. 3I and J), revealing that they are mainly composed of a chromium(m) sulphatebased compound (see also^{19,20} for further details about μ XANES results).

Together with the development of the beamline instruments, additional plug-ins are continuously integrated into the freely distributed PyMca software,¹⁶ in particular for analysis of spectroscopy data sets.²¹ Of particular interest for ID21 are the fast fitting option, statistical tools (principal component analysis, and non-negative matrix approximation), the image realignment tool (for 2D-XANES acquired in both transmission and XRF mode) and the possibility to fit XANES spectra as a user-defined combination of Gaussian and/or Lorentzian

peaks, plus arctangent function(s) for the baseline. Besides, the possibility to use the same software for the data generated at the four ID21 end-stations (μ XRF maps, μ XRD maps, μ FTIR maps and 2D-XANES maps) and in particular cross-correlation of the analyses when acquired simultaneously (same map and pixel dimension), *e.g.* μ XRF combined with μ XRD, is particularly powerful.

2.3. The "XANES full-field" end-station

The XANES full-field instrument is located downstream of the SXM, connected to the SXM chamber through a vacuum valve (cf. Fig. 2, right part).⁵ It is operated in the same energy range, under vacuum (using the same vacuum system as that of the SXM), but without the use of any focusing optics. Stacks of X-ray radiographs of a thin (\sim 5–50 μ m, depending on sample composition and X-ray energy) sample are acquired, while tuning the X-ray energy across the absorption edge of the element of interest. It offers a spectroscopic characterization similar to that of the SXM, but in imaging mode, generating millions of XANES spectra in a single scan (one spectrum per radiograph pixel). The spatial structures of the beam due to imperfect optics are smoothed upstream of the sample by employing an X-ray decoheror (rotating graphite and/or paper foil). Samples are mounted vertically, perpendicular to the beam which dimensions are defined by slits (up to \sim 1.5 mm). The detection system consists of a scintillator (Lu₂SiO₅:Tb, 10 µm thick) located less than 2 mm from the sample to limit phase contrast features. The support of the scintillator is directly mounted on the viewport holder of the detector that ensures the air-vacuum interface. A CMOS PCO.edge camera coupled to a long working distance optical objective records the magnified transmission image of the sample. A 10× or 20× objective can be used, yielding a pixel size of $0.65 \times 0.65 \ \mu m^2$ or $0.32 \times 0.32 \ \mu\text{m}^2$ and a field of view of 1.5 \times 1.5 mm^2 or 0.75 \times 0.75 mm², respectively when combined with the scientific CMOS camera (PCO.edge). The set-up is also compatible with the in-house developed CCD FReLoN E2V camera. Tens of samples can be mounted at once and adaptors have been designed to allow the full-field sample holder to be mounted at the other end-stations. Data are analyzed using the PyMca software or the TXMwizard software package²² while the Spectrocrunch library performs the dark and flat-field correction and the image alignment much like the multispectral µXRF above discussed. As illustrated in the example about blue decors on Chinese porcelains, the full-field set-up is increasingly used to study ceramics.^{23,24} In this kind of materials, the large field of view with high lateral resolution can be employed to obtain insights into firing technologies. The same set-up has also been successfully used to detect the nature and distribution of CdS-based pigments and corresponding degradation compounds in fragments from a series of paintings by Henri Matisse.25

2.4. The scanning µXRD/µXRF end-station

The most recently built instrument (open to users in June 2015) is the μ XRD/ μ XRF end-station, installed on the X-ray sidebranch (Fig. 4). Its implementation was motivated by the many



Fig. 4 Schematic top view of the scanning μ XRD/ μ XRF end-station at ID21. Scales are not real. Volumes in light grey represent vacuum chambers.

experiments performed as a combination of ID21 µXAS and μFTIR with μXRD at another beamline (cf. Table 1). Downstream the ML system and secondary slits, a channel-cut Si(111) monochromator cooled with N2 gas flow is used to obtain a monochromatic beam at an energy of 8.53 keV ($\Delta E/E = \sim 2 \times$ 10^{-4}). The monochromator crystals can be removed from the X-ray beam path to operate with a pink beam ($\Delta E/E = \sim 10^{-2}$). The beam can be focused down to \sim 0.7 μ m (ver.) \times 1.0 μ m (hor.) with a flux of 4 \times 10¹⁰ ph s⁻¹ (monochromatic beam at 200 mA SR current) using a Kirkpatrick-Baez mirror system, operated under a N2 flow. The sample is mounted vertically, perpendicular to the beam, in air, and is raster scanned during acquisition of 2D µXRD/µXRF maps. For this purpose, a combination of stepper and piezo motors similar to the ones allocated in the SXM are used. µXRD patterns are recorded using a taper FReLoN detector (2048 \times 2048 pixels, pixel size 52 μ m). The position of the detector can be adjusted in the horizontal and vertical directions to adapt the required d-spacing range. The maximum 2-theta angle collection with the camera as close as possible to the sample (\sim 3 cm), centered in beam axis, is typically 50° (corresponding to 1.72 Å). The XRF signal is detected by means of an 80 mm² SDD detector (AXAS-M, from Ketek) using a XIA-XMAP digital pulse processor. The sample-XRF detector distance and the angle between the incident beam and the SDD detector can be adjusted. Two visible light microscopes are available, one at fixed geometry (presenting a view of the sample along the beam) and one with variable orientation (from 90° to 30° with respect to the incident beam). Data processing of XRD data is done by PyFAI²⁶ and XRDUA27 software packages. This end-station complements the ID21 spectroscopy instruments by offering specific information about the identification of crystallized phases. As shown in the example of Chinese porcelains (paragraph 3.1.1), this technique may help to provide a more accurate identification of the composition of pigments and of the corresponding degradation products. It has recently been successfully used in combination with µFTIR to identify reaction products of oil with PbO driers.28

2.5. The scanning FTIR microscopy end-station

The scanning FTIR microscope installed at ID21 is a commercial instrument: thermo nicolet nexus infrared bench associated with an infrared Thermo Continuµm Microscope.³ As an alternative to the internal Globar source, a collimated and bright synchrotron beam can be used. At ID21, the edge radiation emitted from the short straight section (focusing electron lenses) upstream of the bending magnet is extracted by a flat un-cooled aluminum mirror with a horizontal slot. This 5 mm slotted-aperture lets the energetic part of the synchrotron light go through for absorption 2.5 m further down. The extracted beam is transferred and shaped into a collimated beam, using a succession of 12 mirrors. The microscope can operate in different configurations: transmission, reflection or Attenuated Total Reflection (ATR) mode. The standard applications include molecular identification and 2D mapping, with a beam size of 5-10 μm. Data are usually analyzed using OMNIC or PyMca as software. This instrument is particularly useful to study organic materials, being in paintings,²⁹⁻³¹ in varnishes covering music instruments32 but also in polymer-based design objects33 or for the analysis of biological materials.34 Moreover, it can be used to study inorganic materials, e.g. alteration of silicate glass.35 The FTIR kinetic study of oil-lead compound paint systems has motivated the integration of additional plugins under PyMca, for the determination of rate laws (by assessing zero, first or second order reactions) and the Arrhenius plot.21

2.6. Ancillary equipment and sample preparation

In addition to these different end-stations, other instruments are available to users at ID21 for the preparation and precharacterization of their samples. Thin sections can be prepared using a motorized rotary microtome (Leica RM2265) equipped with a binoculars microscope for observation of the cutting process, in dry conditions. With this instrument, the section thickness setting ranges from 0.25 to 100 μ m. For applications related to cultural heritage, sections are usually prepared at room temperature, but a cryo chamber is also available for cryo-sectioning, with particular interest for biological samples.

Considering (i) the importance of sample preparation for the success of experiments, (ii) the fact that XANES-full-field, μ FTIR and μ XRD should preferentially be carried out on thin sections, (iii) the complexity of this preparation in the particular case of analysis of artistic materials, specific effort has been made to develop optimized protocols for the preparation of thin sections from painting fragments.³⁶⁻³⁸ The two available protocols, "sample enclosing system" (SES) and "AgCl resin embedding" (ARE), aim at limiting the risk of preparation of the sample,

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i.e. dissolution, oxidation or contamination, during the sample preparation) and the risk of analytical interferences (avoiding spurious signals from the exogenous materials used for the sample preparation). A particular challenge is to avoid the presence of organic embedding media in the sample when analysing the organic components used in paintings. The developed protocols were successfully employed to identify and localize different organic binders in fragments from Ming dynasty painting sculptures at Shuilu'an temple, China.²⁹

The pre-characterization of samples can be done at the beamline using a visible light microscope (Zeiss Axioplan 2) and an electron microscope (TM-1000 Hitachi).

Finally, tools were recently developed to transfer coordinates from one microscope to another. A set of points recorded on one microscope can be transferred to another instrument, through the use of fiducials. As seen in the examples below, most of the micro-analyses involve combination of different microscopes, and this tool speeds up the localisation of the regions of interest.

3. Review of recent cultural heritage related applications

3.1. Revealing ancient artistic and craft practices

In most cases, the esthetical value of glasses, ceramics or paintings result from optical effects (*e.g.* opacity, iridescence, metallic shine or colour). Such effects can be induced by the presence of specific compounds such as opacifying crystals, ionic chromophores or metallic nanoparticles. The oxidation state of elements and more generally their chemical environment is directly correlated to these optical effects. Thus, historical glass and ceramic production methods required adequate control of firing conditions (temperature, atmosphere and time), as well as the introduction of oxidizing or reducing ingredients. Colouring variations are usually obtained in ceramics and glass by modulating the oxidation states of transition elements (such as Cr, Mn, Fe, Co, and Cu) due to their characteristic absorption frequencies in the visible region as a result of d–d electronic transitions. The energy range at ID21 (2.0–9.2 keV) is therefore very well suited to reveal the chemical state of these elements. The extension to slightly higher energies (from 7.3 keV to 9.2 keV) was accordingly important, providing access to other relevant transition elements, in particular Co and Cu.^{39,40} XANES is an ideal technique to probe element speciation in amorphous glasses and/or in pigment micrometric grains. The following three examples show how insights into ancient manufacturing processes can be obtained thanks to micro-analyses.

3.1.1. Mastering colouring effects in ceramics. A series of recent studies at ID21 focused on ceramic samples, ranging from Greek and Roman black and red productions (pre-Sigillita, Campanian²⁴ and Berlin painter sherds²³) to more modern manufacture. As an example, Fig. 5 summarizes a combined µXRF, µXRD, µXANES (in full-field and micro-focussed mode) analysis of blue pigments in Chinese Oinghua porcelains of the Ming dynasty (1368–1644 AD).⁴⁰ The objective was to assess the relationship between colour (blue tint and intensity), macroscopic elemental composition (measured with XRF instruments, directly onto the surface of porcelain sherds) and microscopic elemental and chemical composition determined on fragments prepared as transversal thin cross-sections. For the ID21 analyses, small fragments were sampled from sherds and prepared as thin sections (Fig. 5, top left). µXRF maps show particular concentration of Co and Ca in the blue pigment regions and of Fe on the surface, which could be correlated to different blue tint and intensity (Fig. 5, bottom left). Full-field XANES at the Co K-edge reveals the presence of two main Co species, in the pigment and in the glaze, both being bivalent with tetrahedral coordination (Fig. 5 centre). Finally, the µXRD analysis was used to obtain further information about the Co



Fig. 5 Analyzing the origin of the colour in Chinese Qinghua blue decors (Ming dynasty) by a combination of μ XRF, full-field XANES at Co K-edge and μ XRD at ID21. Fragments were sampled from sherds and prepared as thin cross-sections (Top left). μ XRF maps show particular concentration of Co and Ca in the pigment regions, and of iron on the surface (Bottom left). Full-field XANES at the Co K-edge reveals the presence of two main Co species, in the pigment and in the glaze (middle: (a) transmission image recorded at 7670 eV, (b) absorption edge jump map, (c) cluster maps and average XANES spectra obtained by PCA, (d) speciation maps obtained from the least squares linear combination fitting (standards CoAl₂O₄ and Co in glaze)). μ XRD offers further determination of Co pigment lattice parameters (right) (adapted from ref. 40).

pigment lattice parameters, and revealed the increasing of lattice parameters of the spinel structure, compared to the reference CoAl₂O₄ (Fig. 5 right). This successful multi-microanalytical technique experiment motivated the extension of the work to a larger corpus, including other dynasties, in particular the earlier Yuan dynasty (1279-1368 AD), in order to see how the manufacturing of blue decors and the source of cobalt ores evolved through history. In this example, the full-field XANES set-up proved to be particularly well suited providing both large fields of view and micrometric resolution. Imaging capabilities are required to image chemical variations from the enamel to the pigment particle scale. µXRD, now available, offers a more precise identification of phases, giving access to lattice parameters and consequently to further hypotheses with respect to the firing conditions and the purity of ingredients used in the production.

Another experiment was carried out to understand colour alteration occurring during manufacturing of pink decorations at the famous Sèvres manufacture (Fig. 6).^{41,42} The purpose was to explain in chemical terms the modification of colour which is observed when pigments composed of the spinel solid solution $ZnAl_{2-x}Cr_xO_4$ are fired in an uncoloured frit commonly used at the manufacture. Those pigments were notably synthesised between the end of the 19th and the beginning of the 20th C. and were used to decorate vases belonging to the Art Nouveau style. In the studied process, the initial powdered mixture of the pigment $ZnAl_{2-x}Cr_xO_4$ (x = 0.41) and an uncoloured frit turned into a brown glaze during firing (Fig. 6B). The experiment started with the acquisition of Cr K-edge XANES spectra of pure synthetic references of $ZnAl_{2-x}Cr_xO_4$ pigments, with x varying from 0.2 to 2. For such acquisitions, a "large" (unfocused) beam of 200-300 µm is well suited. Changes in the pre-edge and postedge spectral features can be observed with the Cr content x and put in relation with variations of colour (Fig. 6A) and UV-visible spectra.⁴¹ In particular the appearance of a γ peak in the pre-edge for high Cr content was attributed to the presence of Cr-Cr pairs: the peak corresponding to electric dipole transitions to the p states of the absorbing Cr, orbitally mixed with the 3d orbitals of the neighbouring Cr. In a second step, micro-analyses were carried out on polished cross-sections of porcelain sherds (Fig. 6B). The porcelain presented here was prepared following historical recipes. A mixture obtained by the addition of 10 wt% pigment to an



Fig. 6 From macro to micro XANES characterisation of Cr speciation in $ZnAl_{2-x}Cr_xO_4$ pigments. (A) Macroscopic study of reference powders, synthesized with different *x*, from 0.2 to 2.0; left: visible picture of the powders showing colour variation; right: XANES spectra (edge and preedge) regions, with identification of the main peaks (*cf.*⁴¹ for the assignments of these peaks); (B) Left: description of preparation of glaze samples and subsequent cross-section; right: SEM images of the enamel layer and zoom on a Cr rich pigment grain, embedded in a glassy matrix; (C) Left: μ XRF map of the Cr pigment grain (Cr (red), Al (green) and Si (blue)); right: μ XANES spectra acquired in the core (pt1) and in the periphery (pt2) of the pigment grain, showing the different speciation of Cr in the different central and peripheral areas of the grain (adapted from ref. 41 and 42).

uncoloured frit is painted on the porcelain. The applied thermal treatment (1000 °C reached in 10 h, then 1280 °C reached in 5.5 h) enables the uncoloured frit to vitrify and the glaze to adhere to the porcelain sherd. A cross-section is cut from the porcelain and polished. For the X-ray micro-analyses, the beam was focused down to $0.2 \times 0.7 \ \mu\text{m}^2$. Analyses concentrated on Cr rich pigment grains, pre-located by scanning electron microscopy (SEM) (Fig. 6B). µXRF maps confirmed a particular distribution of Cr and Al in pigment grains, as already observed by SEM. Al is concentrated in the core while Cr tends to distribute around the grain. Furthermore, µXANES performed at several points of such grains revealed a different Cr speciation in the core and in the periphery of the grain, the former being rather similar to that of the initial pigment, the latter showing higher similarities to the features that are visible in the spectra obtained from reference powders with higher Cr content (equivalent to x = 1.4). The modification of the chemical environment of Cr during the dissolution of the pigment in the glaze explains the final colour observed on the porcelain. This example is a typical illustration of the advantage of the high throughput of ID21, in particular for the acquisition of references (typically 1 min per sample) combined with the sub-micrometric imaging capabilities.

3.1.2. Introduction of metals in inks used on papyri. From Antiquity until the 4th and 5th C., ink is said to be mainly carbon-based. The recent successful application of phasecontrast imaging to "read" letters in rolled carbonized papyri from Herculaneum motivated to further explore this hypothesis and to assess the possible presence of metals (which could be then exploited for increased contrast).43 µXRF maps were acquired on two millimetric flat fragments, where Greek letters were vaguely visible. The experiments showed the presence of lead44 and the concentration values of this element determined by Monte Carlo simulations argued in favour of a voluntary introduction of lead into the ink, rather than uncontrolled contamination.45 For such studies, a clear advantage of the ID21 (over macro XRF or SEM-EDX) is the possibility to switch easily from mapping at the letter scale (beam size $\sim 100 \ \mu m$) to mapping at the pigment particle scale (beam size $\sim 0.5 \mu m$) (cf. Fig. 7). The former gives a clear image of the elements present in ink; the later offers additional clues about chemical form through assessment of elemental co-localisation at the

micron scale. In this particular case, the identification of lead phosphates can be inferred, in agreement with recent analyses of one archaeological black powder sampled from a glass vessel found in Pompeii.⁴⁶ The significant results obtained on only a few studied samples suggest that this approach may be applied more widely in future. μXRD will probably give access to fundamental information regarding the nature of these metallic compounds, and will contribute to determine if they were used for colour and/or for drying purposes, and if a link can be established between the chemical compositions and specific (in time and space) manufacturing processes.

3.2. Saving cultural heritage for future generations

In parallel with the discovery of lost artistic practices, a large number of works aim at understanding the evolution of these materials with time. Most of the alteration processes, e.g. metal corrosion, involve modification of the redox states of the original material, while the average elemental composition of the bulk material remains unchanged. The alteration process is usually limited to a highly superficial area, with typical thickness in the micrometer or even sub micrometer range. Nevertheless, such surface changes can have effects on the objects visual appearance. Probing the oxidation of specific elements and more generally their chemical environments is therefore highly relevant when studying alteration mechanisms. This field is intensively studied at ID21. Indeed, the accessible energy range (2.0-9.2 keV) allows the study of: (i) 3d transition metals, being in pigments, glasses, inks or metals as well; (ii), Cl and S species (e.g. SO_2), which are common exogenous species responsible for degradation and corrosion. In parallel, some experiments focus on modern organic based artistic materials, for which the use of µFTIR microscope provides valuable information.

The two examples here below reported are related to the study of artistic materials (organic and inorganic) introduced during the 19th C and requiring specific attention with respect to their instability.

3.2.1. Degradation in organic-based modern artistic objects. Together with the introduction of new inorganic pigments in artists' palettes (see next section), the 19th C. and



Fig. 7 Zoomed analyses of papyri. Determination of ink elemental composition in a fragment of Herculaneum papyrus, by micro XRF mapping. From left to right: step size of 100, 10, 5 and 1 μm; beam size: 100 μm diameter for the first map, and 0.3 μm ver. 0.7 μm hor. for the last three maps. The micron co-localisation of Pb and P supports the presence of a lead phosphate compound. Adapted from ref. 44.

principally the 20th C. saw an explosion of new petroleum-based organic substances, developed primarily for industrial purposes but which immediately found applications in art and design. The variety of these modern materials makes the conservation of contemporary cultural heritage objects even more complicated. Over the last five years, various experiments were carried out at ID21 in this field. μ FTIR was used to analyse fragments from 50's Italian design objects (made of ABS and PVC) as well as model, artificially aged fragments of the same polymers in order to assess the molecular modifications of the material induced by light.³³

Another study was carried out through collaboration between ESRF, the Centre of Research and Restoration of French Museums, Paris, and private curators working for the Rodin museum. For the exhibition Portrait-making, Rodin and his models (2009), the Rodin museum wanted to restore two busts of Hanako and Clemenceau. The observation of these two sculptures revealed the presence of modern modelling materials (MMMs), invented at the end of the 19th C. as an alternative to clay or waxes. In parallel to the restoration of the sculptures, fragments of MMMs were sampled from 12 sculptures and studied with both laboratory techniques (SEM, FTIR, gas chromatography, XRD) and synchrotron-based µXRF, µXANES, µFTIR47 and µXRD (unpublished data) at ID21. Two main MMM compositions could be identified. Analyses at ID21 permitted a more specific analysis of degradation features, such as yellow fatty patina, black dust as well as crystallized aggregates made of Na₂SO₄. As shown in Fig. 8, the fatty aspect of the yellow patina covering the surface is due to both the absence of calcium carbonate (originally present in the paste as shown by the maps of Ca and $CaCO_3$) and the higher concentration of Ca, and probably Mg and Na fatty carboxylates in the superficial layer. The additional presence of wax in these regions cannot be excluded.

3.2.2. Composition and photo-stability of 19th C. pigments. The development of innovative painting materials (new pigments, new formulations, tin paint tubes...) in the 18th C. and particularly in the 19th C. revolutionised painting techniques, offering painters additional possibilities. The variety of paint chemical compositions exploded. However, in impressionist and early modernist paintings from the turn of the 20th C., synthetic inorganic pigments have started to undergo chemical and physical degradation phenomena ranging from fading and colour shifts to spalling and flaking. At ID21, experiments are usually carried out on both well-preserved and altered micro fragments from iconic paintings (for example by V. van Gogh,48,49 J. Ensor,50 H. Matisse,25,51 E. Munch) and from artificially aged model paints. They synergistically aim at determining (i) the original chemical composition of the pigments used by the artist and potentially the corresponding manufacturing recipes and (ii) the environmental parameters (light, pollutants, humidity, temperature...) which can influence the degradation processes of these materials. The chemical modification of pigments often results in a dramatic modification of their colour. Notably for sulphide-based pigments such as cadmium yellows (CdS, Cd_{1-x}Zn_xS),^{25,50,51} cinnabar/vermilion (HgS),52-55 orpiment (As2S3) and realgar (As₄S₄),⁵⁶ the chromatic alteration is usually associated with an oxidation of sulphides into sulphates or substitution by other environmental anions such as chlorides or oxalates. XANES is a very efficient method to probe these modifications at both the macro and sub-micron scale.

Recently, many experiments focused on composition and stability of chrome yellow pigments ($PbCr_{1-x}S_xO_4$). Reproductions of chrome yellow recipes from the archive of the famous paint manufacturer Winsor & Newton showed that the choice of chromate source, sulphate source, lead source and use of



Fig. 8 Identification and study of degradation of modern modelling materials in sculptures by A. Rodin. (A) Clemenceau, bust (S.01982, Musée Rodin, height: 50 cm, length: 34 cm, width: 32 cm), during its laser cleaning (the right and top parts have already been cleaned). Photo credits: H. Bluzat, A. Cascio, and G. Mary. (B) Visible picture showing the different degradation features (yellow efflorescence, yellow and gray colorations on the original ivory-coloured modelling material). (C) Sample preparation (compression between two diamond windows, without any embedding) of a fragment obtained from Two figures embraced on a pillar (Deux figures enlacées sur un pilier; S.05703). (D) μ XRF fitted maps (red: Ca, green: Na, blue: Mg) and (E) μ FTIR region-of-interest (ROI) maps (red: calcium carbonates, ROI: 1623–1302 cm⁻¹; green: calcium carboxylates, ROI: 1593–1550 cm⁻¹) acquired from the pressed sample shown in (C). (F) FTIR spectra from points 1–3, as shown in (E). Adapted from ref. 47.

different additives and extenders may strongly impact the final composition, colour and photo-stability of the pigments.⁵⁷

The photo-stability is usually assessed by exposing paint model samples (with more or less complex compositions) to different lights (from monochromatic illumination to commercial white sources). In the case of chrome yellows, these experiments have permitted to elucidate that the photo-stability of the final paint strongly depends on the chemical composition and crystalline structure of the chrome yellow and on the environmental conditions (*e.g.*, light, temperature, humidity) to which the pigment is exposed to.^{19,57-61} Notably, the surface of the paint composed of the highly substituted PbCr_{1-x}S_xO₄ (x > 0.4) orthorhombic phase darkens significantly after artificial photo-ageing while that made of monoclinic PbCrO₄ show a slight colour change (Fig. 9A).⁵⁸⁻⁶⁰ Higher photo-stability could be associated with the highest solubility of S-richest orthorhombic phases relative to that of the S-free/ poorer monoclinic phases.^{59,62} Observation of cross-sections of these model samples under visible light showed that the degradation layer is limited to a few microns of the paint surface (Fig. 9B). μ XANES analyses were carried out at both the Cr and the S K-edges to tackle any chemical modification in the 3–4 μ m thick degradation layer. XANES at S K-edge did not show any particular reduction of the SO₄^{2–}. Conversely, the Cr chemical state maps (Fig. 9C) and the quantitative Cr(vI)/Cr(m) depth profiles obtained *via* linear combination fitting of the Cr K-edge μ XANES spectra acquired from the photo-aged PbCr_{0.2}S_{0.8}O₄ model paints (Fig. 9D and E) demonstrated without any doubt the reduction of the original Cr(vI) into Cr(m)-compounds and revealed that the highest relative abundance of reduced Cr (up to about 60%) is localized in the upper 3–5 μ m of the paint.^{58–61}

In parallel, similar measurements have been also performed on a series of minute fragments obtained from darkened



Fig. 9 Study of the degradation of chrome yellow pigments in artificially aged model paints. (A) Photographs of PbCrO₄ and PbCr_{0.2}S_{0.8}O₄ paints before and after exposure to different commercial lamps. (B) Microphotograph of a PbCr_{0.2}S_{0.8}O₄ thin section aged using a UV-filtered xenon lamp and (C) corresponding RG composite Cr(vi)/Cr(iii) chemical state maps [step sizes (hor. × ver.): $0.8 \times 0.3 \,\mu\text{m}^2$; dwell time: 100 ms per pixel]. The dotted white rectangle in (B) shows the area where data of (C) were recorded. (D) Quantitative Cr(iii)/Cr(vi) depth profiles obtained as a result of (E) the linear combination fitting (red) of PbCr_{0.2}S_{0.8}O₄, Cr(OH)₃/Cr₂O₃ and/or Cr(iii)-organo-metal compounds/Cr₂(SO₄)₃·H₂O to the line profile of XANES spectra (black) obtained from the region shown in (C) (adapted from ref. 60).



Fig. 10 Study of the degradation of chrome yellow pigments in Van Gogh paintings. (A) Photograph of Sunflowers by Van Gogh (Arles, 1889; Van Gogh Museum, Amsterdam, NL) and sampling spot of micro-fragment F458/4. (B) Photomicrograph detail of sample F458/4 and corresponding (C and D) RG composite $Cr(v_i)/Cr(w)$ chemical state maps [pixel size (hor. × ver.): $0.7 \times 0.2 \mu m^2$; dwell time: 100 ms] recorded from two regions of interest as shown in (B). (E) Cr K-edge μ -XANES spectra acquired from the areas shown in (C and D). Green labels indicate the relative percentage amount of Cr(w) obtained as a result of the linear combination fitting of different Cr-reference compounds XANES profiles to the spectra obtained from the sample (adapted from ref. 49).

chrome yellow areas of a series of paintings by Vincent van Gogh (Fig. 3 and 10; see also^{19,20,48,49} for additional details).

Cr-speciation investigations of a micro-sample (F458/4) taken from the light-yellow table of the Sunflowers (Van Gogh Museum, Amsterdam, NL; Fig. 10A and B) provide clear indications for the presence of reduced Cr inside the varnish layer and at the varnish/paint interface. At one location (Fig. 10C), Crrich particles are completely reduced to Cr(III) and the corresponding µXANES spectrum (Fig. 10E: pt 014-I) points to the presence of Cr₂O₃. In the surrounding area, the relative abundance of Cr(m) is about 50% (pt 02_{4-1}). In another region (Fig. 10D), around 35% of Cr(III)-species are present as a thin layer (2-3 µm thickness) at the varnish/paint interface, while only Cr(vi)-compounds have been identified in the yellow paint underneath (Fig. 10E: pts 01_{4-II}-02_{4-II}). This pattern is very similar to that observed in light-sensitive PbCr_{0.2}S_{0.8}O₄ model paint, suggesting that a color change arising from the reduction of the original chrome yellow pigment has occurred (cf. Fig. 9C and 10D).

3.2.3. Health and environmental concerns of metallic pigments. In addition to their in/stability, an important concern with modern (and traditional) pigments is their potential toxicity. As an example, in 1855, M. J. Lefort proposed to classify pigments depending on their toxicity, in four classes: (1) "dangerous colours", *e.g.* arsenic based pigments, (2) "less dangerous colours", *e.g.* lead based pigments, (3) "weakly poisonous colours", *e.g.* ochre.⁶³ Out of the limited field

of artistic materials, the potential in/direct toxicity of paints in everyday life (household paint, vehicle paint, road paint) is a major concern. ID21 instruments are regularly used in the field of environmental sciences to evaluate any possible effects of dispersion of metals and nano-materials in the environment.64-66 This can be done for example by exposing organisms directly to a metallic ion solution (e.g. deposit of solution on plant leaves, intravenous injection or intratracheal instillation in animals) or indirectly, (e.g. through growth of plants in a contaminated soil). The metal can then be mapped at the sub-cellular scale in different plant organs, to detect any specific accumulation or transfer and its chemical environment can then be probed with µXANES in order to evaluate any possible chemical modifications of the initial pollutant (e.g. reduction, complexation). This is fundamental since the chemical state of the metal will dramatically impact its future toxicity, in particular in the food chain. Such measurements benefit from the same advantages as applications in the field of cultural heritage, namely simultaneous detection and distribution mapping of both low Z elements (e.g. Na, P, S, Cl, K naturally present) and metals of interest, with sub-micrometric resolution; together with a large field of view, chemical sensitivity thanks to XANES and the possibility to probe molecular modification thanks to µFTIR. In addition, these studies take full advantage of the cryo-stage which allows the analysis of cryo-prepared sections, offering a better preservation of fragile organic tissues and a reduction of risk of radiation damage. Besides, they fully exploit the high detection limits. While this is rarely critical when studying paints, realistic simulation of exposure of organisms to contamination requires



Fig. 11 Study of sunflower plants exposed to Cr^{VI} in hydroponic media at 10 ppm for 72 h. Portions from the roots, stems and leaves were sampled, cryo-fixed and cryo-sectioned (30 μ m) and analysed at ID21 under cryogenic conditions. Left: pictures of the cryo-microtome and cryo stage. Middle: scheme of the samples location and Cr μ XRF maps. Right: Cr K-edge μ XANES spectra from references Cr^{VI} solution and Cr^{III} malate compared to the average spectra from the points marked in the Cr μ XRF maps.

the use of very low concentrations, which are even more diluted after uptake by the plants. Accordingly, high flux and high detection sensitivity are fundamental. Such SR cryo-studies of interactions between paints (or more generally artistic materials) and bioorganic systems (fungi, plants) are still limited in the field of cultural heritage, but may be strongly considered in the future, based on very successful applications in the field of environmental sciences. As an example, Fig. 11 shows the results from analysis of sunflower tissue cryo-sections (root, stem, and leaf) of plants exposed to Cr^{VI} in hydroponics. Cryogenic conditions are necessary to preserve elemental distribution, within an intact tissue structure, but especially to retain the initial Cr oxidation state. µXRF mapping reveals the distribution of Cr in the plant tissues. Of principal interest is the identification of Cr species present in the tissue, the chromate oxy-anion posing a threat to the plant cells by inducing high levels of oxidant stress.⁶⁷ Sunflower plants are able to absorb and fully reduce Cr^{VI} to Cr^{III}, as shown in the µXANES spectra from all plant tissues (Fig. 11). The reduction of Cr^{VI} to Cr^{III} is most likely taking place at the root epidermis layer and from there Cr^{III} is transported bound to small organic acids; Cr^{III} species are also accumulated in cell walls (unpublished data).

4. Conclusions and perspectives

The ID21 beamline evolved substantially since its initial design. It is now a multi micro-analytical platform specialized in 2D multi-chemical imaging. The sub-micrometric resolution in the tender X-ray domain, together with the combined availability of a µFTIR microscope makes it a unique facility. The examples shown in the present review focus on cultural heritage objects, not only highlighting the variety of materials studied and problems tackled but also illustrating how cultural heritage user community takes full advantage of the combination of micro-analytical techniques. In the context of the ESRF-EBS (extremely brilliant source) upgrade, the upgrade of ID21 is currently in preparation. A new source, together with new optics, new detectors and new electronics should deliver a smaller (down to ~100 nm) and more stable beam, and increase the data acquisition speed. For the cultural heritage community this will be directly translated into larger and hence more representative range of applications, larger fields of view, a generalization of XANES hyper-spectral mapping acquisition (instead of multi-spectral maps limited to a few energies) and finally improved lateral resolution, permitting exploration of the artistic materials in finer detail. In addition, an upgrade of the cryo capabilities is also planned, which will be highly beneficial to the study of biological samples. This future stateof-art nanoscope will certainly reveal new secrets about our cultural heritage objects.

Authorship

MC is the beamline scientist in charge of ID21 and has collaborated to all the research projects presented here. She wrote most of the manuscript. LM and KJ planned and performed the research on the degradation of chrome yellow pigments. TW and PS planned and carried out the research on blue decors in Chinese porcelains. LV, LC and OD planned and carried out the research on pigments and glazes composed of spinel $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$ at the manufacture of Sèvres. EB planned and carried out the research on Herculaneum papyrus. NB, YV and JL collaborated in the analyses of modeling materials in Rodin's sculptures.

EP, MS, CR, WdN, HC, TF, BH, AP, GV, BF and JS participate in the development of instruments and in user experiments. In particular, EP took part into the commissioning of the full-field station (with BF), the implementation of innovative sample preparation for combined μ XRD-XRF-FTIR and XANES analyses for Cultural Heritage (with TF), and into the development of data processing approaches used in these works (with VAS and JK). CR participated in the development of the μ XRD instrument, WdN and HC implemented and commissioned the XANES hyperspectral mapping tools. DB, R. Barrett, R. Baker, C. Cornu, C. Cohen, EG, EP are strongly involved in hardware and software developments at ID21.

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