

# TRAINING CAMP

Dalla diagnostica alla fruizione museale: le opere  
del Museo del Colle del Duomo di Viterbo

7 - 13 NOVEMBRE 2021



REGIONE  
LAZIO

## Synchrotron Radiation and Cultural Heritage

Dott.ssa Antonella Balerna



UNIVERSITÀ  
DEGLI STUDI DELLA  
TUSCIA

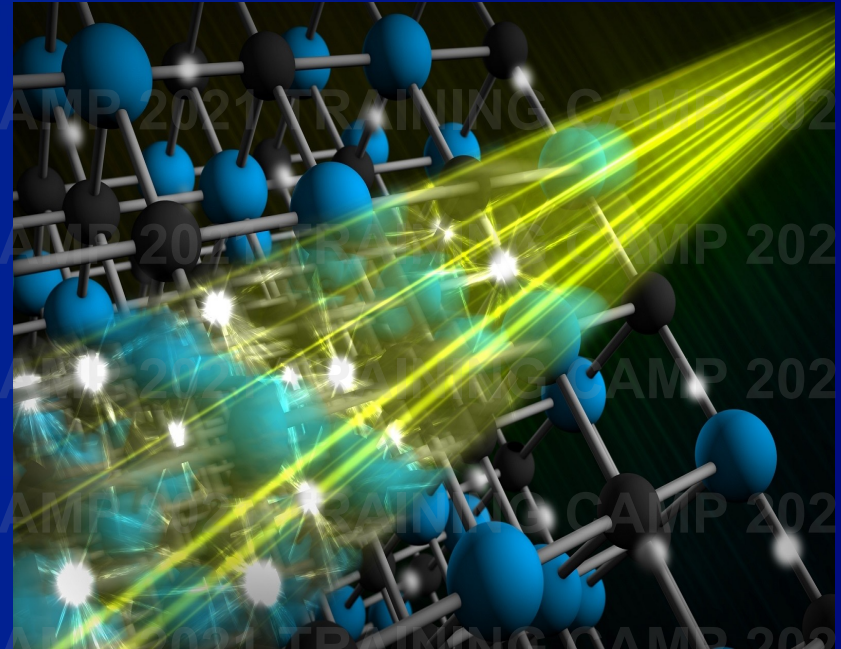


POLO  
MONUMENTALE  
COLLE DEL DUOMO  
VITERBO



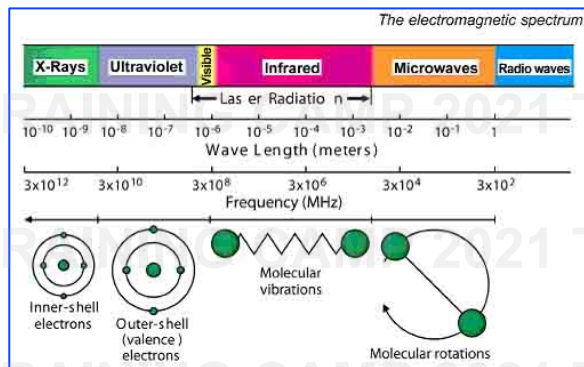
# Synchrotron Radiation and Cultural Heritage

1. Short introduction
2. Synchrotron Radiation (SR)
3. SR and Cultural Heritage
4. Some applications
5. How to apply for beamtime
6. Beamtime and proposals
7. Case study
8. Conclusions

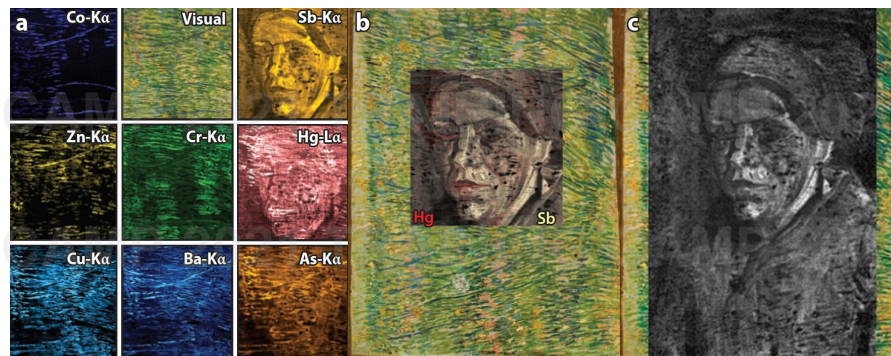
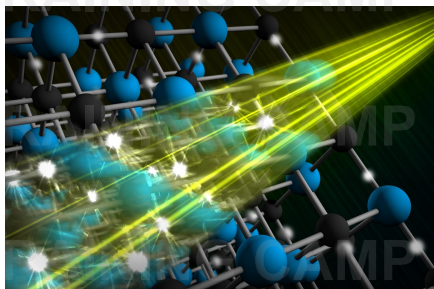


## Short introduction

## Light, material science and cultural heritage



Different wavelengths  
different spectroscopies



Making the invisible  
visible with X-rays

K. Janssens et al. *The Use of Synchrotron Radiation for the Characterization of Artists' Pigments and Paintings*, Annual Rev. Anal. Chem. 2013. 6:399–425  
DOI: 10.1146/annurev-anchem-062012-092702

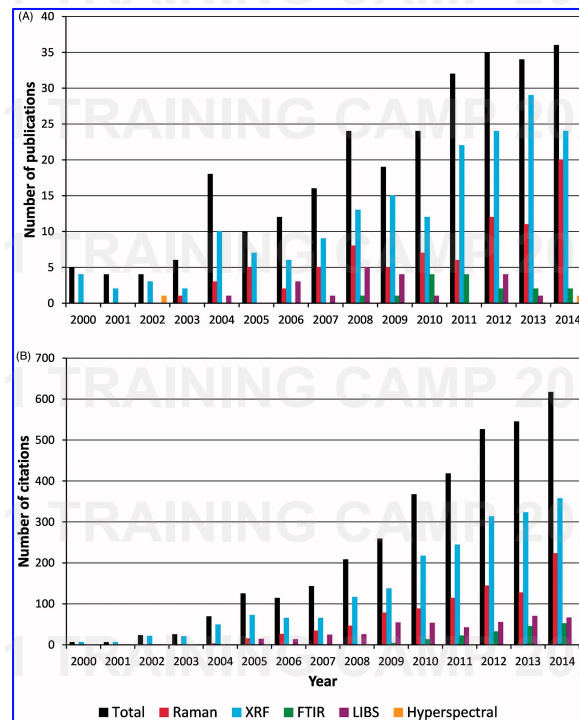


## Portable Laboratory Instrumentation

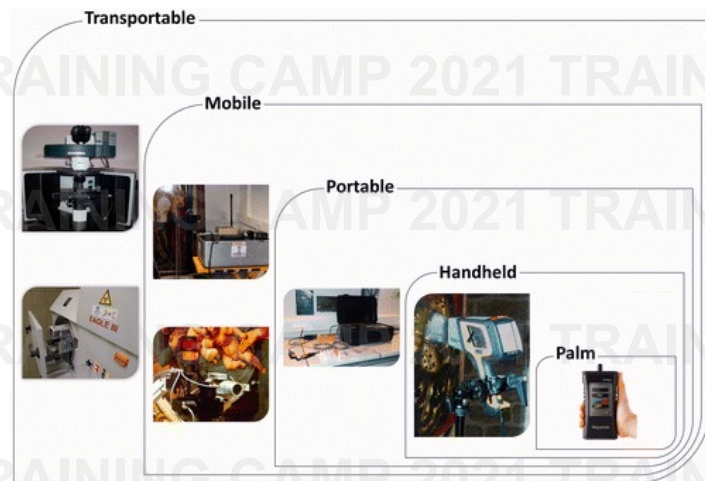
**Laboratory instrumentation** is of growing importance in Cultural Heritage field. Equipment is used **in the field or at museums**, thus **avoiding transportation or risk of damage to valuable artifacts**. Many spectroscopic techniques are **non-destructive and micro-destructive** in nature, which **preserves the cultural heritage objects themselves**.

**Raman spectroscopy, X-ray fluorescence spectrometry, Fourier Transform Infrared spectroscopy** and other techniques are the ones mainly used.

Review of over **160 references** pertaining to the use of **mobile spectroscopy** for archaeometry up to 2014: **P. Vandenabeele, *Mobile Spectroscopic Instrumentation in Archaeometry Research*, *Applied Spectroscopy* 2016, Vol. 70(1) 27–41 - DOI: 10.1177/0003702815611063**

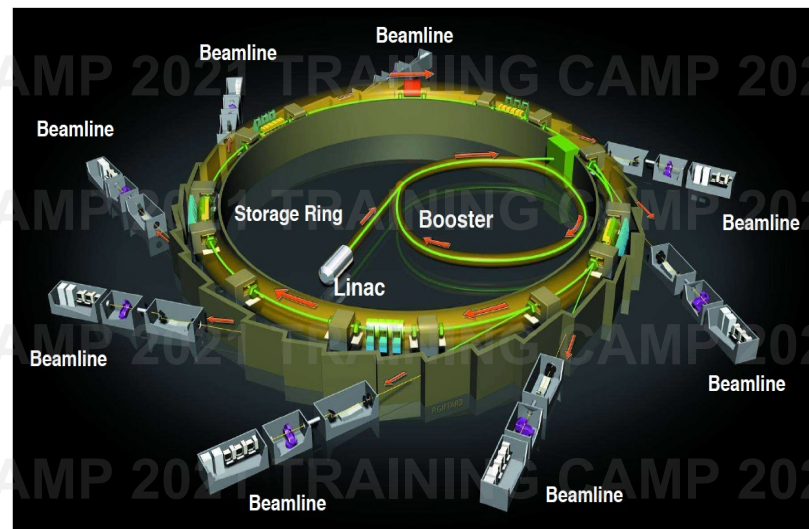


## Moving from portable laboratory to SR-based instrumentation



### Laboratory instrumentation

P. Vandenabeele, *Mobile Spectroscopic Instrumentation in Archaeometry Research*, **Applied Spectroscopy** 2016, Vol. 70(1) 27–41 - DOI: 10.1177/0003702815611063



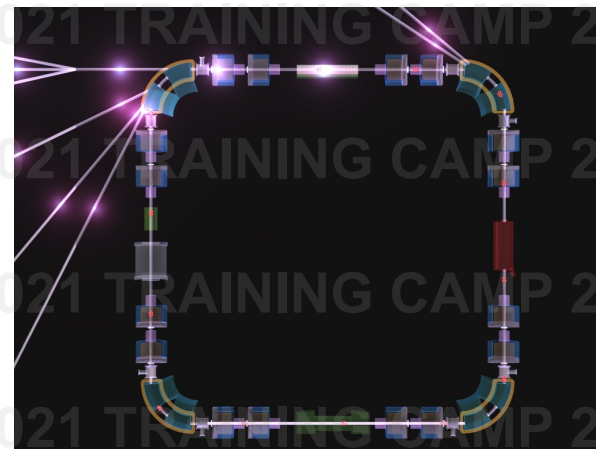
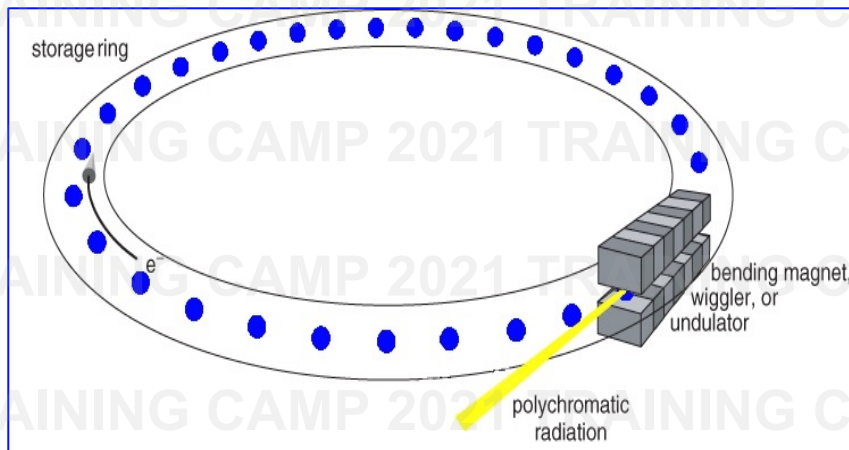
### Particle accelerators as light sources for studies in different fields

# Synchrotron Radiation



## What is synchrotron radiation?

The term “**synchrotron radiation**” refers to the electromagnetic radiation – **x-rays, ultraviolet, visible and infrared** – emitted by **high-energy electrons circulating in a particle accelerator**. Specifically, the accelerators used in modern facilities are “storage rings” in which the electron, accelerated to **nearly the speed of light** and forced to move on **circular paths by bending magnets** emit Synchrotron Radiation – that is collected by several beamlines and used for different experiments.

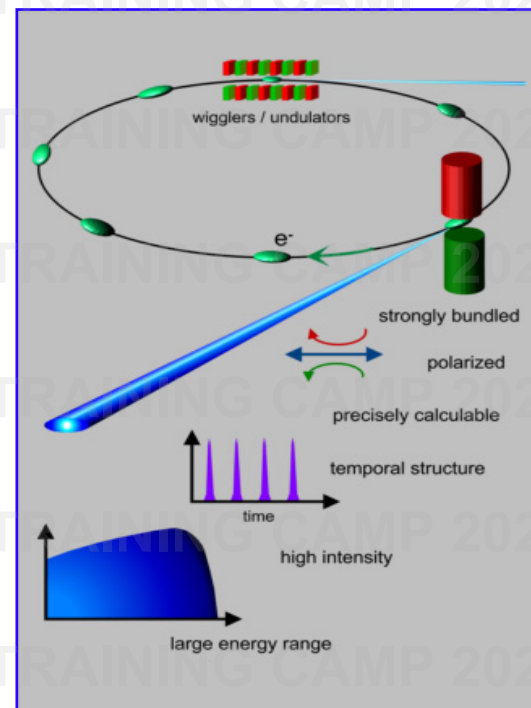




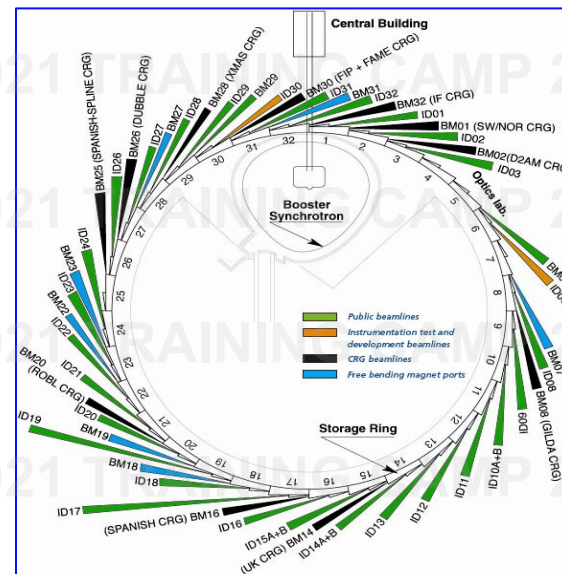
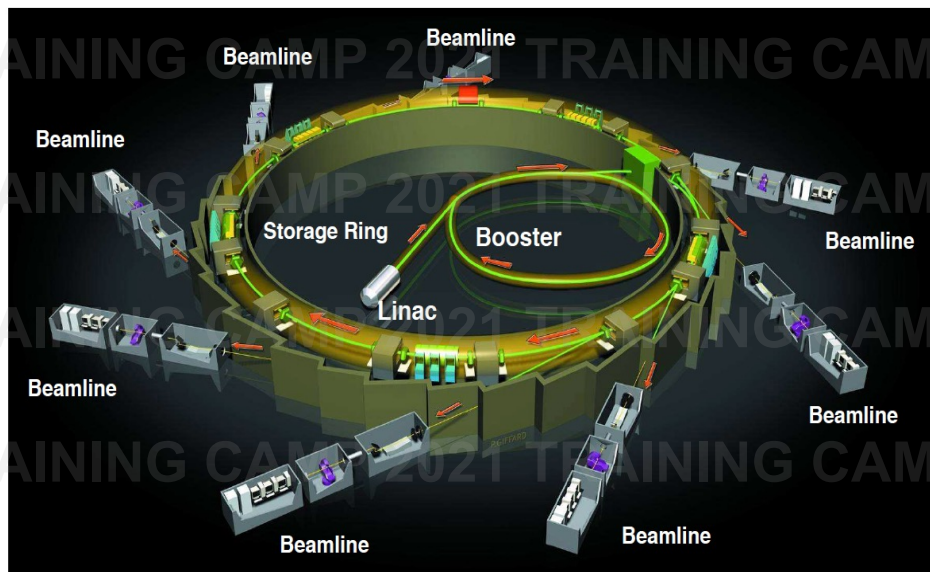
## Synchrotron radiation properties

**Synchrotron radiation has important properties:**

- a **bright beam**, which permits **fast acquisitions**, with **improved detection limits**, which translate into wider corpus, wider fields of view, **higher representativeness of the results** and **higher sensitivity**;
- a **collimated beam**, which permits to focus the beam to the **micron range**, and **even smaller** with **state of-the-art nano-probe beamlines**. This is particularly important considering the **heterogeneity of artistic materials**;
- an extended and almost **continuous energy range**, which gives access to **X-ray spectroscopy**. This technique is particularly relevant for the analysis of artistic materials since it **probes element speciation, which is usually altered during object manufacturing or degradation**. Information **about chemical reactions involved throughout the entire life of the works of art** can thus be obtained. Beside, synchrotron radiation also gives access to lower energies and spectroscopy performed in the **UV/Visible** and the **Infrared domains** can offer **complementary characterization tools**.



## Synchrotron radiation facilities



Schematic views: ESRF, Grenoble - France 6 GeV,  
C = 844 m opened to users in 1994

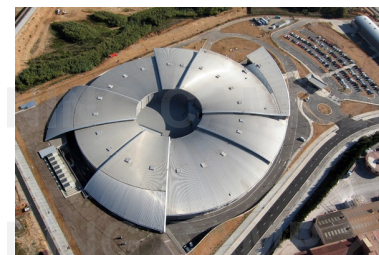
## Synchrotron radiation facilities



**ESRF - France**



**DIAMOND - UK**



**ALBA - Spain**



**Lund - Sweden**

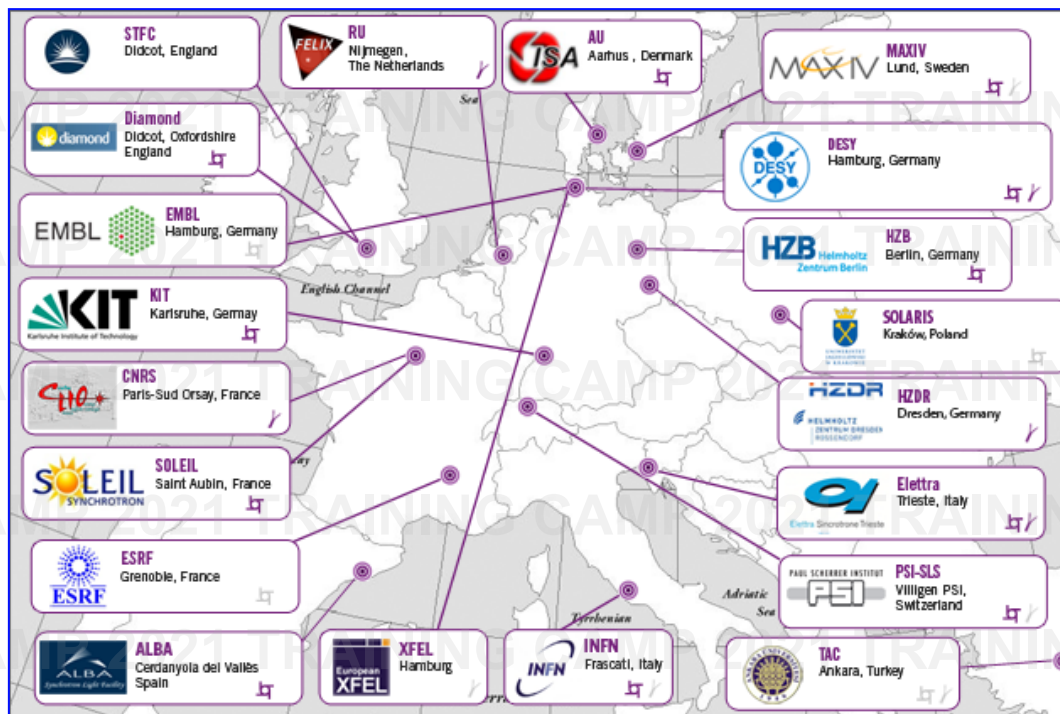


**Sirius - Brazil**



**Shanghai - China**

## Synchrotron radiation facilities and Europe



<http://www.calipsoplus.eu/>

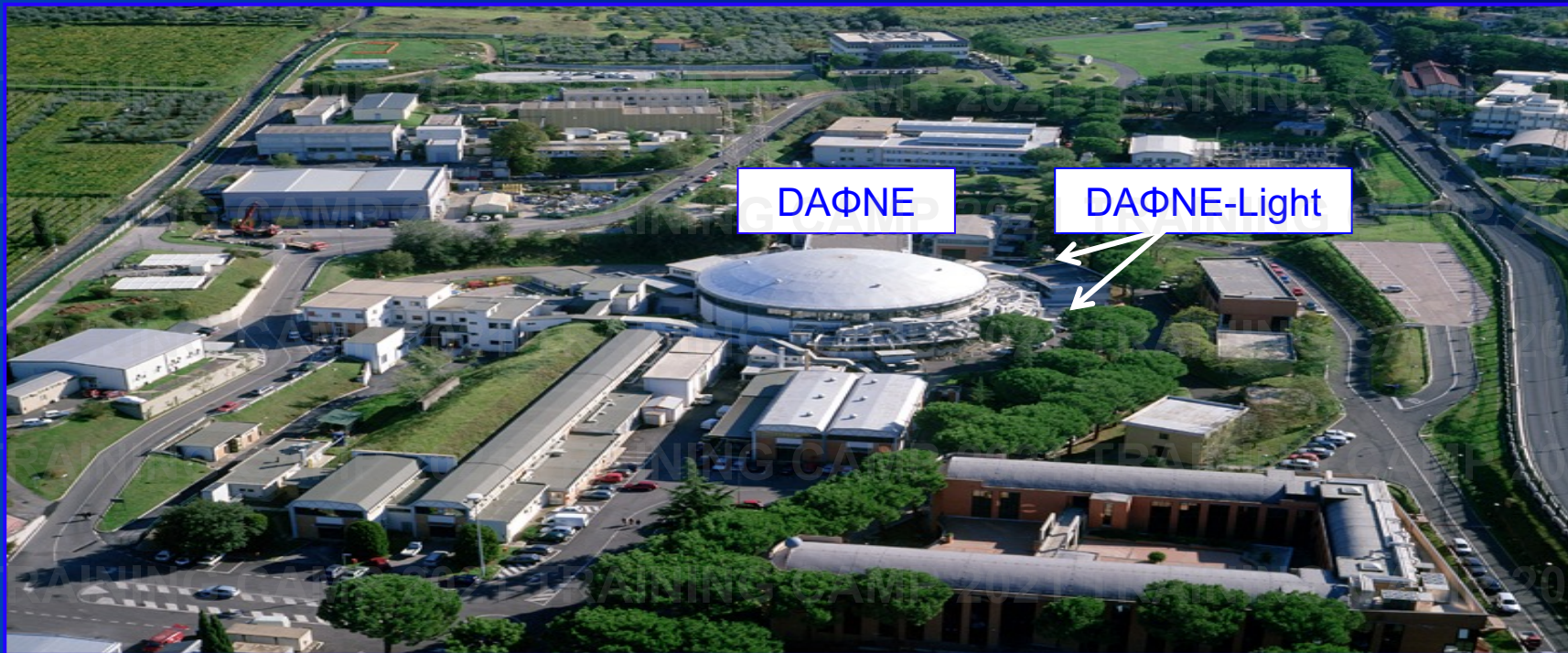


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# DAΦNE-LIGHT

## INFN-LNF Synchrotron Radiation Facility

## INFN Frascati National Laboratory



## Beamlines @ DAΦNE-Light

### OPEN to USERS

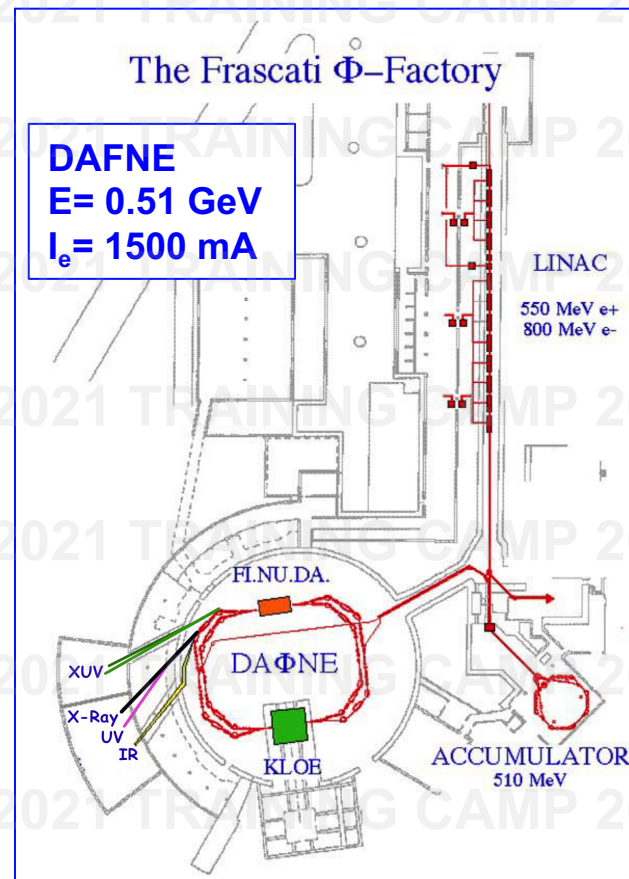
- 1) SINBAD - IR beamline (1.24 meV - 1.24 eV)
- 2) DXR1- Soft x-ray beamline (900-3000 eV)
- 3) DXR2 – UV-VIS beamline (2-10 eV)

### XUV beamlines UNDER COMMISSIONING

- 4) XUV1 - Low Energy Beamline (30-200 eV)
- 5) XUV2 - High Energy Beamline (60-1000 eV)
- 6) New XUV2 Branch White Line -WINDY

### Call for proposals (two/year) deadlines:

- 20 June
- 18 December



## Techniques available at DAΦNE-Light

- **FTIR spectroscopy, IR microscopy and IR imaging - BS Mariangela Cestelli Guidi**
- **UV-VIS absorption spectroscopy - BS Marco Angelucci**
- **Photochemistry: UV irradiation and FTIR micro-spectroscopy and imaging.**
- **Soft x-ray spectroscopy: XANES (X-ray Absorption Near Edge Structure) light elements from Na to S - BS Antonella Balerna**
- **SEY (secondary electron yield) and XPS (X-ray photoelectron spectroscopy) – by electron and photon bombardment - BS Roberto Cimino**



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# Synchrotron radiation and Cultural Heritage

## Synchrotron Radiation as a powerful tool

### Questions often asked on artifacts:

- 1) what material is it made of ? or Composition
- 2) when was it realized? or Dating
- 3) where was it made? or Provenance
- 4) how was it made? or Art Technology
- 5) how can we avoid its damaging? or Conservation

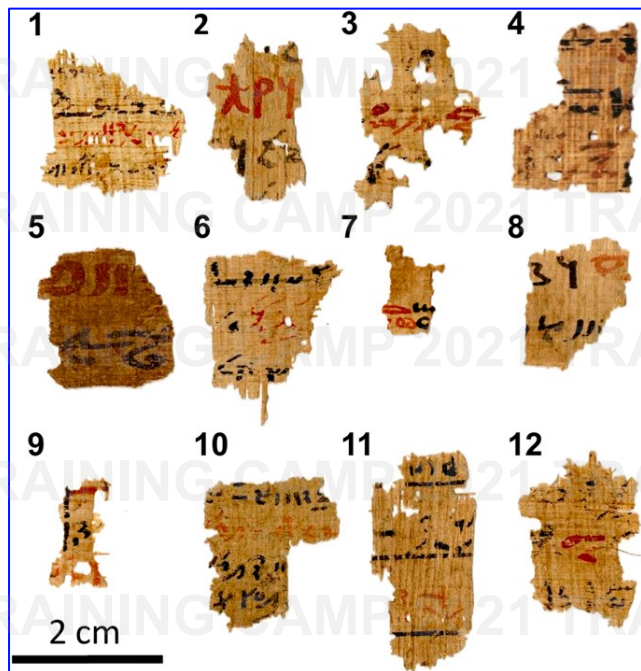
### Some investigations that can give answers using SR and X-rays:

- 1) Elemental microanalysis down to the sub-ppm level using of X-ray fluorescence analysis ( $\mu$ -XRF).
- 2) Local chemical state determinations of selected (trace) constituents using XAS and  $\mu$ -XAS (X-ray absorption spectroscopy)
- 3) Imaging of entire objects using high energy SR to allow high quality radiographic or tomographic measurements, revealing the internal structure of these artifacts.

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Some applications

# Ancient Egyptian red and black inks on papyri and $\mu$ -XRF



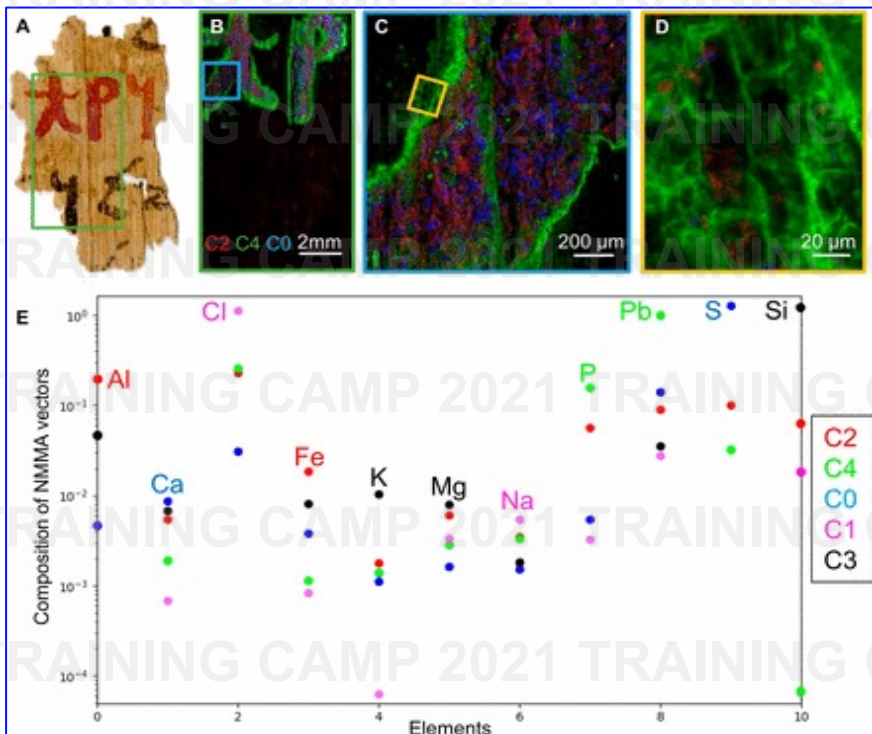
Ink, invented in ancient Egypt circa 5,000 y ago, is the established and time-honoured medium where with human kind commits words to writing. A comprehensive **synchrotron-based microanalysis of a considerable corpus of ancient Egyptian papyri from the Roman period**, inscribed with red and black inks, reveal a **hitherto undetected complex composition of inks**. Highlighted by the **presence of iron**, the **red colour can be attributed to the use of ochre**. Unexpectedly, **lead is regularly present in both the red and black inks** and is associated to phosphate, sulphate, chloride, and carboxylate ions. The analysis shows that **lead was probably used as a drier rather than as a pigment**, similar to its usage in 15th century Europe during the development of oil paintings.

**$\mu$ -XRF**

T. Christiansen et al. Proceedings of the National Academy of Sciences  
Nov 2020, 117 (45) 27825-27835; DOI: 10.1073/pnas.2004534117



## Ancient Egyptian red and black inks on papyri and $\mu$ -XRF



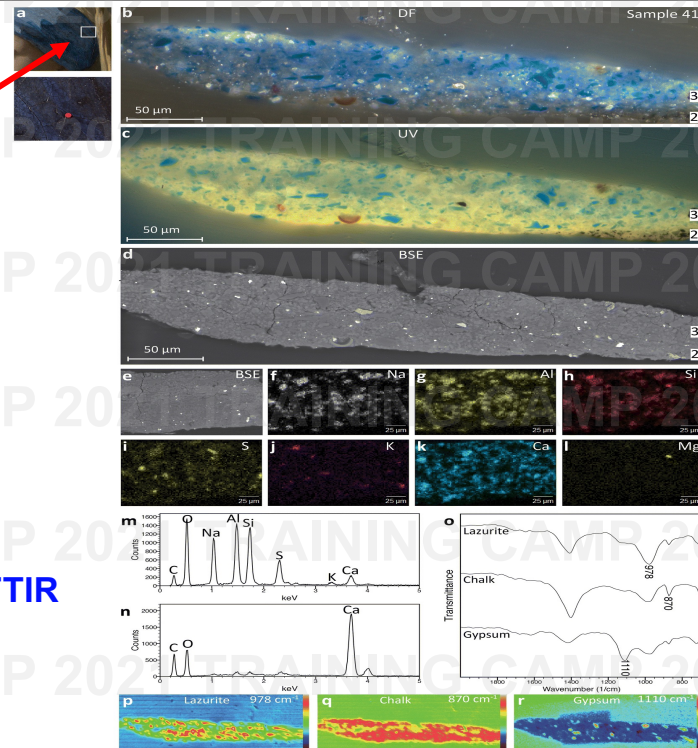
(D)  $\mu$ -XRF map (yellow rectangle in C). E = 2.9 and 8.7 keV. **Beam size: 0.54  $\mu$ m horizontal  $\times$  0.75  $\mu$ m vertical**. Area size: 140  $\mu$ m horizontal  $\times$  140  $\mu$ m vertical. Step size: 0.7  $\mu$ m horizontal  $\times$  0.7  $\mu$ m vertical.

**Synchrotron-based microanalysis ( $\mu$ -XRF) can give important information thanks to the beam properties!**

## Out of the blue: Vermeer's use of ultramarine and XAFS



Micro-sampling



XRF and FTIR

By Johannes Vermeer *Girl with a Pearl Earring*

<https://www.mauritshuis.nl/>, Public Domain,

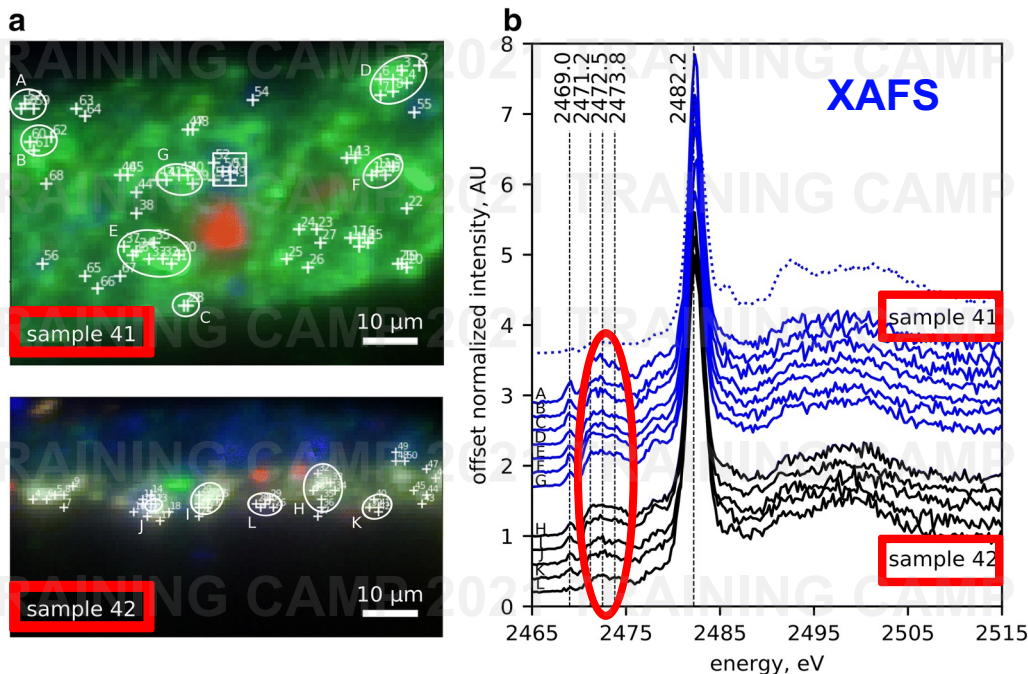
<https://commons.wikimedia.org/w/index.php?curid=55017931>

A. van Loon et al. *Herit Sci* (2020) 8:25

<https://doi.org/10.1186/s40494-020-00364-5>

## Out of the blue: Vermeer's use of ultramarine and XAFS

### Sulphur K edge XANES or X-ray Absorption Near Edge Structure



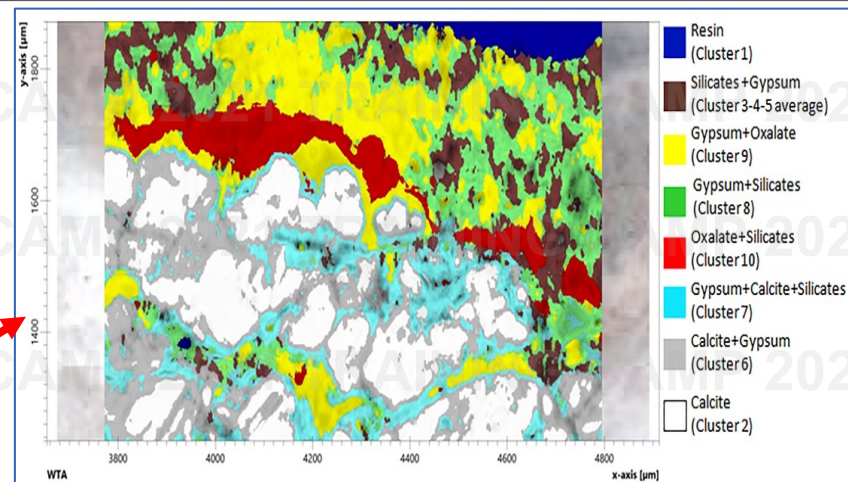
Analysis with synchrotron sulphur K-edge XANES suggested that the **ultramarine pigment was prepared- at least in part- from a heat-treated lapis lazuli rock.**

The relative ratio of peaks within the 'envelope' region- namely those at 2471.2, 2472.5, and 2473.8 eV - indicate the **influence of heat-treatment**. It was recently found that for lazurite extracted from **lapis lazuli heated at 600 °C** the relative intensity of the peak at 2471.2 eV was greater than that at 2472.5 and 2473.8 eV



## Degradation products in artwork cross-section and FTIR

Among the different analytical techniques, FTIR imaging provides information on the Molecular Composition of the Material on a micrometric-scale in a **NOT DESTRUCTIVE** way. Establishing the distribution of materials and that of their degradation products in historical monuments/paintings is fundamental to **understand their CONSERVATION STATUS and give information for ART RESTORATION.**



**Small fragment of Septimius Severus's Arch - Foro Romano (III AD) new perspectives for FTIR imaging in Art Conservation for the study of the distribution of different components.**

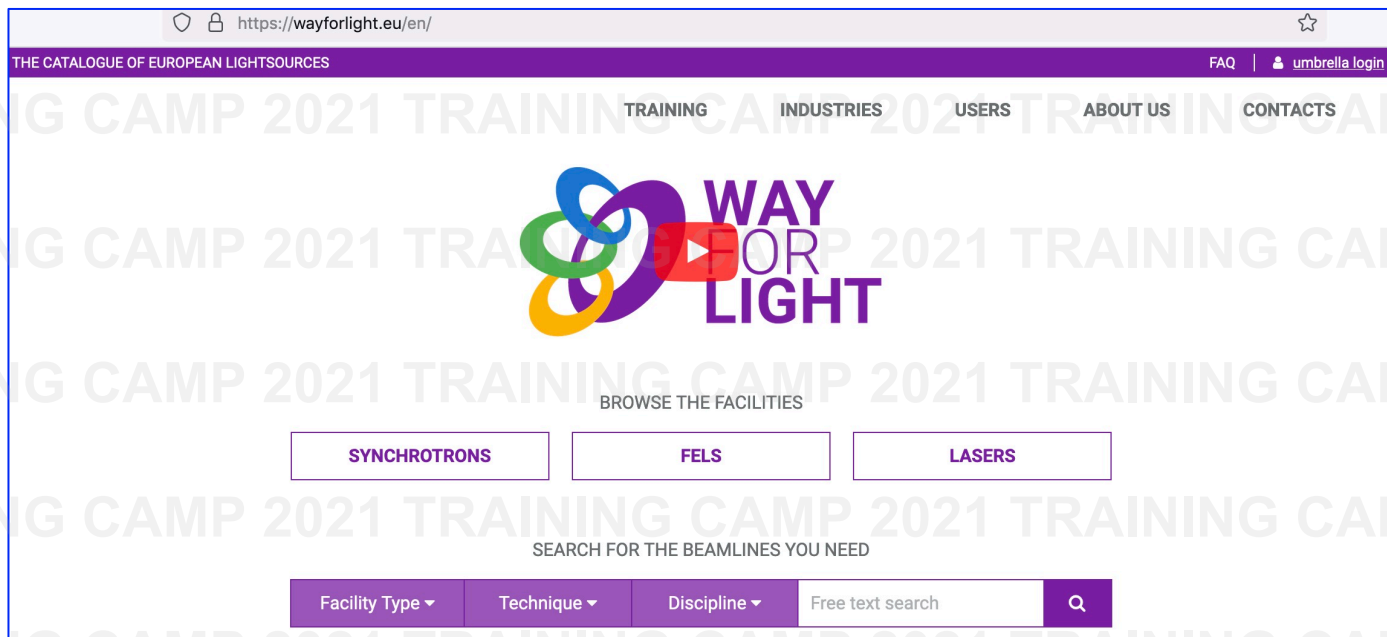
G. Capobianco et al. *Microchemical Journal* (2017) 132,69  
<https://doi.org/10.1016/j.microc.2017.01.007>



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How to apply for beamtime

# WAYFORLIGHT or Catalogue of the EU Light sources



<https://wayforlight.eu/en/>

## WAYFORLIGHT and Cultural Heritage

https://wayforlight.eu/en/synchrotrons

THE CATALOGUE OF EUROPEAN LIGHT SOURCES

WAY FOR LIGHT

Facility Type \* Technique \* Diagnostic \* **Cultural heritage**

INDUSTRIES USERS ABOUT US CONTACTS

SYNCHROTRONS FILLS LASERS

### SYNCHROTRONS

**ALBA**  
CERN, Spain

ALBA is a third generation synchrotron light source facility, designed to provide a high brilliance photon beam. It is co-financed by the Spanish Government and the regional Government of Catalonia, and managed by the Consortium for the Construction, Equipment and Exploitation of the Synchrotron Light Laboratory (CELESL). The accelerator complex consists of a 100 MeV Linear Accelerator (LINAC),

**ASTRID2**  
Aarhus, Denmark

ASTRID2 is the new third-generation low-emittance light source at Aarhus University, Denmark. Commissioned in 2013, the new facility provides state-of-the-art high-brilliance light from the beamline electron beam, operating in top-up mode to give an infinite beam lifetime.

**BESSY II**  
Berlin, Germany

The third generation storage ring BESSY II is in operation since 1999 and provides ultrashort photon beams from the long wavelength Tautz ring to hard X-ray with complete control of the energy range and the polarization of the radiation. The facility is operated by the Helmholtz-Zentrum Berlin.

**DAΦNE**  
Frascati (RM), Italy

DAΦNE Light is the Synchrotron Radiation Facility at the INFN Frascati National Laboratory. The radiation source DAΦNE is an electron-positron collider that works at 0.5 GeV with beam currents higher than 1 A in operation since 1998.

**Diamond**  
Bucks, Oxfordshire, England

Diamond is a 3rd Generation 3GeV synchrotron light source which has a 1940V linear accelerator (LINAC) and full energy (1940V's 3GeV) Booster. Top-up mode became available in 2008. Diamond has been operating since January 2007, when the first 7 beamlines became operational. By the end of 2012 the number of operational beamlines increased to 22, with 32 operational by 2018.

**Elettra**  
Trieste, Italy

The third-generation electron storage ring Elettra, operated by the Elettra Laboratory of Sincrotrone Trieste S.p.A. since 1993, leads 27 beamlines. Researchers from more than 50 different countries, selected by an international committee on the basis of the quality of their scientific proposals, access the facility each year.

https://wayforlight.eu/en/catalogue/

WAY FOR LIGHT

TRAINING INDUSTRIES USERS ABOUT US CONTACTS

Cultural heritage

EXPLOIT OUR BEAMLINES AND FACILITIES CATALOGUE AND ITS SMART FILTERS! DISCOVER THE CATALOGUE

WATCH THE VIDEO

8 BEAMLINES IN 7 FACILITIES

**SYNCHROTRONS**

**FILLS**

**LASERS**

SEARCH

BESSY II  
DAΦNE  
ESRF  
Elettra  
MAX IV  
SSESAME

**OPERATIONAL BEAMLINE**

Operational beamline 7

**TECHNIQUES**

Absorption 4  
Diffraction 2  
Emission or Reflection 6  
Imaging 6  
Ion Spectroscopy 0  
Lithography 0  
Photoelectron emission 4  
Scattering 1

**DISCIPLINES**

Chemistry 3  
Earth Sciences & Environment 4  
Energy 4  
Engineering & Technology 1  
Humanities 1  
Information & Communication Technology 1  
Life Sciences & Biotech 4  
Material Sciences 2  
Mathematics 1  
Physics 3  
Social Sciences 0

**SAMPLE TYPE**

4

**SYNCHROTRON BESSY II**  
Berlin, Germany

**IR-Spectroscopy and -Microscopy - IRIS**

IRIS Thz/Infrared Dipole Beamline. At synchrotron light sources of the second and third generation the emitted radiation in the ...

**SYNCHROTRON DAΦNE**  
Frascati (RM), Italy

**SINBAD IR**

The beamline operates in dedicated and parasitic regime of the Daphne storage ring with circulating beam current of 1 A average. One ...

**SYNCHROTRON ESRF**  
Grenoble, France

**ID26 - XAS / XES**

ID26 - High-Brilliance X-ray Absorption and Emission Spectroscopy (XAS-XES). ID26 is dedicated to X-ray spectroscopy in the applied ...

https://wayforlight.eu/en/catalogue/Test-cultural-heritage

WAY FOR LIGHT

TRAINING INDUSTRIES USERS ABOUT US CONTACTS

Cultural heritage

EXPLOIT OUR BEAMLINES AND FACILITIES CATALOGUE AND ITS SMART FILTERS! DISCOVER THE CATALOGUE

WATCH THE VIDEO

8 BEAMLINES IN 7 FACILITIES

**SYNCHROTRON Elettra**  
Trieste, Italy

**BL 06.1 R - SYRMEP**

The SYRMEP (Synchrotron Radiation for Medical Physics) beamline has been designed by Sincrotrone Trieste, in cooperation with the ...

**BL 09.1 - SISSI - Bio**

SISSI-Bio is the Chemical and Life Sciences branch of the infrared beamline at Elettra, SISSI (Synchrotron Infrared Source for Spectroscopy) ...

**SYNCHROTRON MAX IV**  
Lund, Sweden

**Balder**

The Balder beamline is dedicated to X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) in medium and hard ...

**SYNCHROTRON SESAME**  
Amman, Jordan

**BEATS**

BEAmeLine for Tomography at SESAME BEATS is an E2020 European project to build a beamline for tomography at the SESAME synchrotron ...

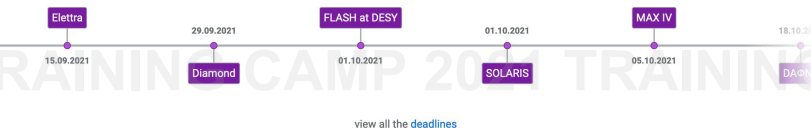
**SYNCHROTRON SOLEIL**  
Gif-sur-Yvette Cedex, France

**SMIS**

SMIS beamline (Spectroscopy and Microscopy in the Infrared using Synchrotron) is dedicated to micro-spectroscopy and imaging. It ...

### WAYFORLIGHT: Deadlines and calls

#### NEXT CALL DEADLINES



#### USERS / NEXT CALL DEADLINES

**SYNCHROTRON**

**Elettra**

**NEXT DEADLINE:**

- September 15<sup>th</sup>, 2021 for experiments to be scheduled from January 1st to June 30th, 2022
- Protein Crystallography: proposals can be submitted anytime, there is no deadline for the submission and evaluation is monthly.

**SYNCHROTRON**

**Diamond**

- First Wednesday in April (17:00) (for the period 1st October 31st March)
- First Wednesday in October (17:00) (for the period 1st April to 30th September).

Details for the next calls for Direct Access and Programme Mode are on the web at: <http://www.diamond.ac.uk/Users>.

In addition to call deadlines specified above, there are also opportunities for rapid access to some beamlines. More details are given on the Diamond website by using the specified link.

**FEL**

**FLASH at DESY**

The deadline for the current call for proposals for FLASH is on 1 October 2021.

Due to the upcoming FLASH2020+ shutdown (from mid-November 2021 to mid-August 2022), this call relates to beamtime from November 2022 to June 2023. In order to facilitate a most efficient use of the FLASH beamtime it is expected that your own experimental setup, if provided, will be ready by November 2022.



STANDARDISED  
PROPOSAL FORM

[read more](#)





## Applying for beamtime

INFN LABORATORI NAZIONALI DI FRASCATI

DAΦNE-LIGHT  
Synchrotron Radiation Facility

Apply for beamtime

HOME BEAMLINES TEAM USERS RESEARCH EDUCATION GALLERY NEWS COVID-19

**Users and Beamtime**

**Apply for beamtime**  
Access, safety, infos  
Organization

**Industry and Services**

Cultural Heritage-CHNet

Quick requests

GDPR and Users

Practical Information

Access Instructions

Before you write a proposal, we advise you to talk to the beamline scientists to discuss the technical feasibility of your experiment. They will help you to decide on the amount of time you will need, and will help you verify if suitable sample environment equipment is available. At the end of the call the proposals will be submitted to the **User Selection Panel (USP)** to determine their scientific merit and to a **Technical Committee** to evaluate their feasibility.

Proposals must be written in English and should include:

- 1/ General Part of the proposal
- 2/ Abstract and experimental description
- 3/ Samples and substances declaration together with ancillary equipment declaration (for safety considerations)
- 4/ Results from previous proposals

When submitting a proposal for a new project or to continue a project for which you have previously been assigned beamtime, you will be prompted to **submit an experimental report** on your past measurements (including relevant publications), before completing your new submission.

[GUIDELINES FOR APPLICATIONS](#)

To send your proposal, you can either download a word file at the following link "Application form DAFNE-Light", fill it in and send it once signed to "proposalsubmission@lists.infn.it" or create it online, following the link below. You will receive a pdf by email so you can check it and send the signed one to the same email address.

[CREATE ONLINE YOUR PROPOSAL](#)

[INFORMATION FOR CALIPSOPLUS USERS](#)

DAΦNE-Light

ESRF  
The European Synchrotron

ABOUT US USERS & SCIENCE INDUSTRY EDUCATION & OUTREACH JOBS

Home -> Users & Science -> Apply for beamtime

APPLY FOR BEAMTIME

Users & Science

APPLY FOR BEAMTIME

ESRF User Portal (SMIS) it

Electronic Submission - Guidelines & Templates

Advice on writing a good proposal

Scientific use of ESRF

Upgrade: Beamline status

Safety Requirements

Long Term Projects - General Information

Allocation of beamtime for Structural Biology

**Next Proposal submission Deadlines**

- Standard and BAG proposals:  
Monday 13 September 2021 (inclusive)  
Guidelines
- IMPORTANT - Test your User Portal login NOW**
- Long Term Project proposals:  
Monday 17 January 2022 (inclusive)  
Guidelines
- Experiment reports submission:  
5th March and 13th September each  
year for reports supporting a new  
proposal. Important - please read!

**Apply for beamtime**

User portal

Beamline status

Find a beamline

Electronic submission: Guidelines

ESRF-EBS

## Beamtime and proposals

## Proposals

- **Abstract or proposal summary**
- **Aims of the experiments and background (scientific background)**
- **Experimental Methods (measurement strategy)**
- **Beamlines and Beamtime requested**
- **Results Expected**
- **References**

**- Main or Principal Proposer and Co-proposers**

**N.B. for any question or doubt concerning the experimental method or required shifts contact the Beamline Scientist**

## Abstract or proposal summary

- The summary will usually be the last thing to write, although it will appear at the beginning.
- Its purpose is the following: reviewers that are forced to read many proposals will not memorize all of them very well.
- You need to give them a very quick way to remember what was your point, in order to allow them to 'defend' your proposal in the review panel meeting, and grade it appropriately.

## Aims of the experiments and background

- You need to explain in a rather compact manner (1/2 page or so) the status of our field, which are the open questions, and what is needed to answer the questions.
- You have to give an introduction in only few sentences, to make the point of what is still *problematic*, *unsolved*, *unknown* and it is also important to show that our sample has already been characterized by as many non-SR techniques as possible.
- Use literature references, but not too many and also refer to your own work on the topic, with or without SR, as well. Since at least a number of the panel members are experts of the field and know the literature, they will get an impression from the references: quoting one or two important references is therefore a good idea, since this indirectly shows our expertise.



## Experimental Methods

- Here you need to explain how measurements will be performed, the instrumentation needed, number and kind of samples to be measured and how you are going to analyse the data.
- Beside the referees also the beamline scientist that will review our proposal to comment whether the proposed experiment is feasible at the chosen beamline.
- The referee needs to judge how experienced you are, how difficult and feasible the experiment is. If it is particularly challenging also this can be very attractive. Synchrotron facilities prefer to host the most forefront experiments.

## Beamlines and Beamtime

- Here you must justify why you ask for a specific beamline, and how much beamtime is required for our experiment.
- The selection of the beamline is sometimes critical, but you already know that a certain beamline is well suited for the proposed experiment.
- The amount of beamtime is another question: while you want as much as possible, asking for unrealistically many “shifts” (typically 8 hours, so one day are three shifts) will rather be seen as a negative aspect of the proposal: reviewers will assume you know how synchrotrons operate and how beamtime is allocated. On the other hand it is clear that certain measurements take some time, you might need to measure at least three samples to get a trend of one parameter, and to ask for one shift extra for setup of the beamline is usually o.k.

## Results Expected

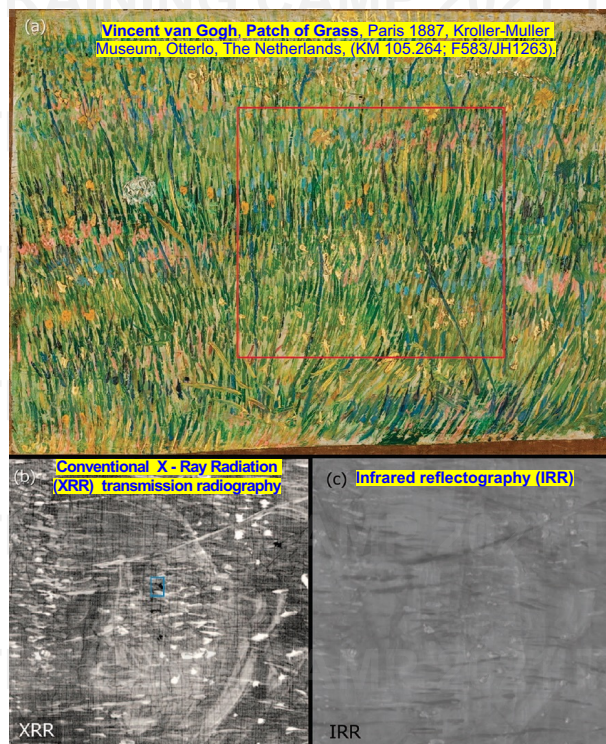
- You need to give a very compact view of what you hope to learn from the proposed experiment. It is better to be very clear and put well-defined, attainable results here. Making a list is not a bad idea, it makes it easier for the reviewers to orient themselves in the proposal.
- A particular problem is to find the balance between important enough results and not overdoing it. Having, in a realistic amount, the larger goal in mind, may help in cases, also to convince the panel with its diverse background that the scientific issue is topical and of a wider interest.

## References

- As mentioned above, references do not serve the same purpose in a short proposal than in a publication. Of course you must refer to the original literature but since you do not have too much space, you can restrict yourselves to a few important papers of the field, high-impact ones and reviews, to show that you know the relevant literature.
- You must also refer to our own publications on the topic, with or without application of SR, to show that you are already experienced (to some extent) in the field, have done previous work (including characterization of the material by in-house, non-SR techniques), know the method etc. All this primarily serves the purpose of convincing the referee that you will manage to perform the proposed work.

## Case study

# Visualization of a Hidden Painting of van Gogh



## Abstract or proposal summary

**Vincent van Gogh (1853-1890), one of the founding fathers of modern painting,** is best known for his vivid colours, his vibrant painting style, and his short but highly productive career.

His **productivity is even higher than generally realized, as many of his known paintings cover a previous composition.** This is thought to be the case in one-third of his early period paintings. **Van Gogh would often reuse the canvas of an abandoned painting and paint a new or modified composition on top.** These hidden paintings offer a unique and intimate insight into the genesis of his works.

### Problem to solve

**Current museum-based imaging tools are unable to properly visualize many of these hidden images.** Using **synchrotron radiation based X-ray fluorescence (XRF) mapping,** recording at a decimetre-scale XRF intensity maps of specific elements in the paint layers, will give the possibility to reveal the distribution of specific elements in the paint layers and bring to the **visualizing a woman's hidden face under the work Patch of Grass by Van Gogh with unprecedented detail.**

### Purpose

This reconstruction can be the missing link for the comparison of the hidden face with Van Gogh's known paintings and **this approach literally can open up new vistas in the non-destructive study of hidden paint layers.**

### Defend your Proposal



# Visualization of a Hidden Painting of van Gogh

## Aims of the experiments and background

**Vincent van Gogh** is generally recognized as one of the founding fathers of modern painting [1]. **In recent decades his work has undergone extensive art historical and technical study.** One striking feature that emerged is **Van Gogh's frequent reuse of paintings in order to recycle the canvas** [2]. The artist would simply paint a new composition on top of an existing work. **This is usually attributed to the artist's lifelong economic hardship and the rapid, energetic evolution of his artistic ideas. Visualizing such hidden paintings is of interest to both specialists in the field of Van Gogh and the public alike.** Covered paintings in general provide an **insight into the making of artworks and the underlying conceptual changes.** In the case of Van Gogh, they also present a touchstone for comparison with preparatory drawings and the abundant literary record. [Background](#)

**Non-destructive imaging of such hidden paint layers is usually realized by means of tube-based X-ray radiation transmission radiography (XRR).** The absorption contrast in these images is mostly caused by **the heavy metal components of pigments employed**, such as lead in lead white or mercury in vermillion. **Conventional XRR, however, has a number of important limitations.** First of all, the observed X-ray absorbance is a summation of all element-specific absorbances. This implies that the contribution to the overall image contrast due to (low quantities of) weakly absorbing elements will frequently be obscured by heavier elements that are present in higher concentrations. Second, prior to the application of the paint layer, a canvas is usually primed with a homogeneous layer of lead white. This raises the overall background of the absorption image derived from the paint layers. Finally, **the polychromatic character of an X-ray tube further reduces the contrast in radiographic images.** As a result, **conventional XRR imaging of paintings frequently provides only a fragmentary view of their substructure, which can severely hamper the readability of hidden compositions** [3]. [Background](#)

The painting by Van Gogh from his 1886-87 Paris period, **Patch of Grass** (Kroller-Muller Museum, Otterlo, The Netherlands) was earlier examined with XRR and infrared reflectography (IRR) **vaguely revealing a head under the surface painting.** However, due to the limitations of XRR, the facial characteristics could not be clearly read, making the person portrayed far from identifiable. Instead of **using the absorption of primary X-rays as an imaging method, one can also record the intensity of secondary radiation, emitted by the atoms in the painting while a pencil beam of energetic X-rays is scanned over the surface.** This fluorescence technique has the added advantage that the emitted X-ray radiation is element specific. The covering surface layers will not significantly attenuate the high-energy fluorescence signals from heavy elements in the hidden layers; in this manner, the distribution of both minor and major components in the painting can be visualized. **The use of high intensity X-ray beams reduces the dwell time for data acquisition to such an extent that large, decimetre- sized areas can be scanned.** [Aims of the experiment](#)

# Visualization of a Hidden Painting of van Gogh

## Experimental Methods

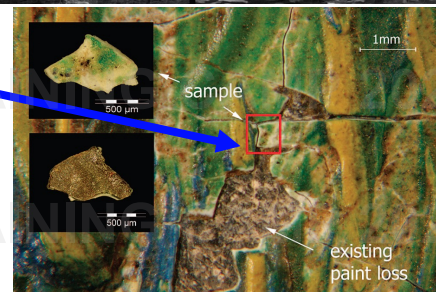
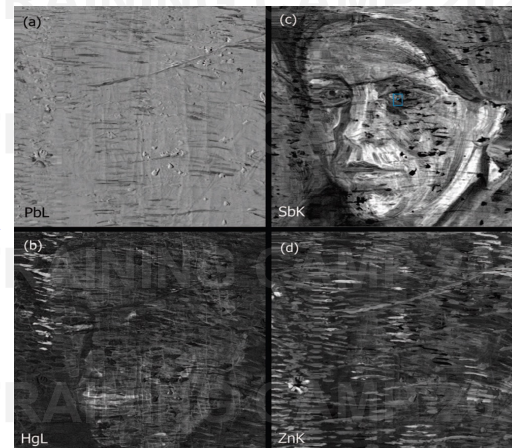
**Safe transport** of Patch of Grass to a micro-fluorescence synchrotron radiation beamline.

A **pencil beam** ( $0.5 \times 0.5 \text{ mm}^2$ ) of **quasi monochromatic synchrotron radiation with an energy of 38.5 keV to be used for primary excitation**. With this beam a square of approximately  **$17.5 \times 17.5 \text{ cm}^2$** , corresponding to the position of the covered head must be scanned. With a **dwell time of 2 s per pixel**, so that the **total scan time was approximately 2 days**. Fluorescence spectra must be recorded for each pixel with a high-resolution energy dispersive Ge-detector.

X-ray Absorption Near Edge Structure (XANES) spectroscopy to learn about its chemical binding of the most relevant elements including standards.

A **microscopic sample must be taken from the painting** in order to study the **elemental composition of the upper and lower paint**. The paint sample will be embedded in epoxy resin to be measured with a SEM microscope with EDS.

As a complement to the high energy measurements performed on the painting itself, the same polished section employed for **SEM analysis** must be used for **characterization by means of low-energy synchrotron X-ray microbeam analysis**. The objective is to determine the elemental components and the correlation of their distribution within the paint layers. Under vacuum,  **$\mu\text{-XRF}$  ( $1.1 \times 0.3 \text{ }\mu\text{m}^2$  /horizontal - vertical) and  $\mu\text{-XANES}$  measurements must be performed** at lower absorption edges for a better **identification of the pigments including standards**.



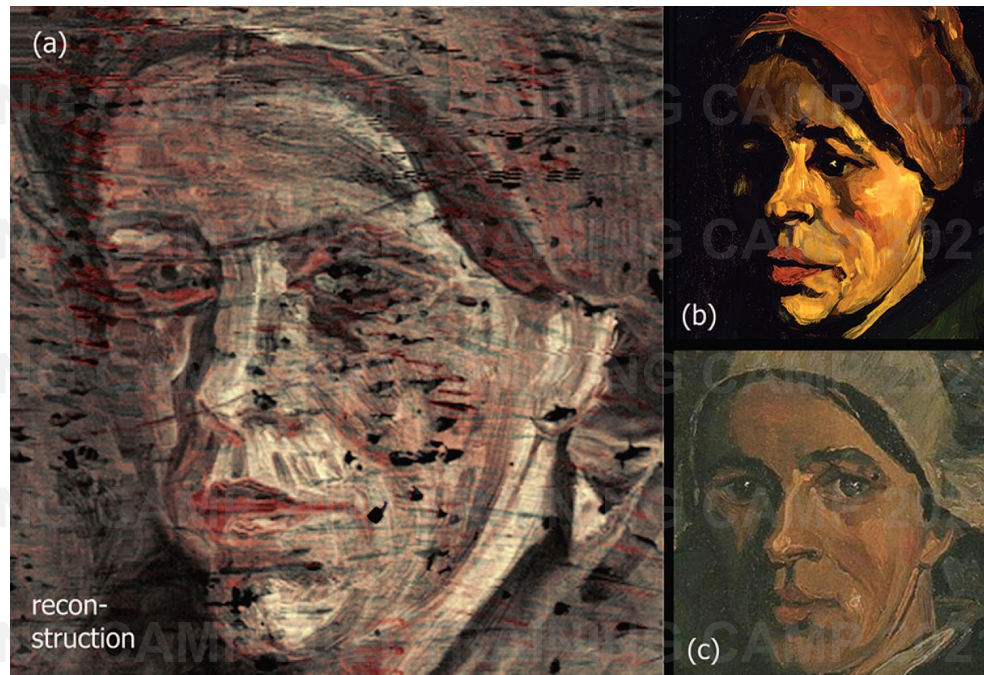
# Visualization of a Hidden Painting of van Gogh

## Results Expected - XRF

- 1) **Elemental distribution images once reconstructed from the resulting sets of peak areas must be compared with features on the surface painting as well as the XRR and IRR images.**

Reconstruction of a significantly clearer and more detailed image of the hidden composition than the XRR and IRR images taken earlier. The brushstrokes and all physiognomic details, such as eyes, nose, mouth, and chin could be visualized. Understand if this reconstruction can prove to be the missing link for the comparison of the hidden face with Van Gogh's known paintings.

(a) **Tritonal color reconstruction of Sb (yellowish white) and Hg (red)** representing the flesh color of the hidden face. (b) Detail from Vincent van Gogh, Head of a Woman, Nuenen, winter 1884-85, oil on canvas, 42 cm  $\times$  33 cm, Kroller-Muller Museum, Otterlo (KM 105.591; F154/JH608). (c) Detail from Vincent van Gogh, Head of a Woman, Nuenen, winter 1884-85, oil on canvas, 42 cm  $\times$  34 cm, Van Gogh Museum, Amsterdam (F156/JH569).



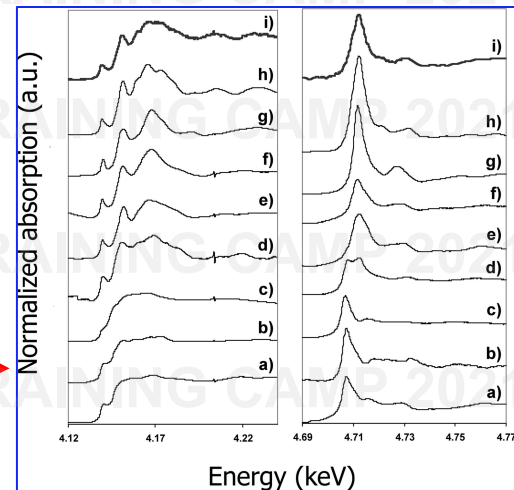
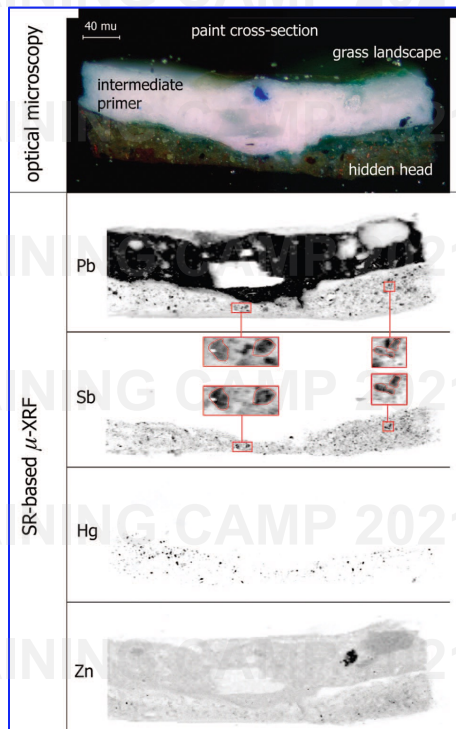


# Visualization of a Hidden Painting of van Gogh

## Results Expected XRF and XANES

2) Determination from the elemental distribution maps acquired by XRF of the most important traced element (probably antimony - Sb) of the hidden layer, measured on the most interesting points of the hidden layer and information using **X-ray Absorption Near Edge Structure (XANES) spectroscopy** on its chemical binding to understand the pigment used.

J. Dik et al., *Visualization of a Lost Painting by Vincent van Gogh Using Synchrotron Radiation Based X-ray Fluorescence Elemental Mapping*, Anal. Chem. 2008, 80, 6436



XANES spectra at the Sb-L<sub>III</sub> edge (left spectrum) and at the Sb-L<sub>I</sub> edge (right spectrum). Reference antimony compounds: Sb<sub>2</sub>O<sub>3</sub> as (a) valentinite and as (b) senarmontite; (c) Sb<sub>2</sub>S<sub>2</sub>O<sub>6</sub>, kermesite; (d) Sb<sub>2</sub>O<sub>4</sub>; (e) Sb<sub>3</sub>O<sub>6</sub>OH, stibiconite; (f) K<sub>2</sub>SbO<sub>3</sub> · 3H<sub>2</sub>O; (g) NaSbO<sub>3</sub> · 3H<sub>2</sub>O; (h) Naples yellow; and (i) Sb pigment in the cross section of the Van Gogh painting.

## Visualization of a Hidden Painting of van Gogh

### Why Synchrotron Radiation ?

- **Portable XRF allows for non-destructive elemental analysis** but has a **rather larger footprint on the painting**.
- It's acquisition **time per pixel is high** (200 s), so that scanning is fairly impossible. **Synchrotron sources have a high brightness and energy range compared to classical sources**.
- **SR-based XRF therefore allows one to quickly scan large, decimeter-scale areas with sub-millimeter spatial resolution, but the painting needs to be transported to an SR facility**.
- SEM has an easy access, has a higher lateral resolution, and probes a thinner superficial layer than SR  $\mu$ XRF. **Vice versa,  $\mu$ XRF has a higher sensitivity, notably for heavier elements. In addition, polychromaticity is essential for  $\mu$ XANES, which complements elemental identification with their chemical characteristics**.

### References

- 1) Hulsker, J. The New Complete Van Gogh: Paintings, Drawings, Sketches; John Benjamins: Philadelphia, PA, 1996.
- 2) Hendriks, E. Van Gogh's Working Practice: A Technical Study. In New Views on Van Gogh's Development in Antwerp en Paris: An Integrated Art Historical and Technical Study of His Paintings in the Van Gogh Museum; Hendriks, E., Van Tilborgh, L., Eds.; University of Amsterdam: Amsterdam, The Netherlands, 2006; pp 231-245.
- 3) Krug, K., Dik, J., den Leeuw, M. *et al.* Visualization of pigment distributions in paintings using synchrotron *K*-edge imaging. *Appl. Phys. A* **83**, 247–251 (2006). <https://doi.org/10.1007/s00339-006-3519-y>



## Conclusions

## Conclusions

- Synchrotron Radiation as a **powerful tool** in the Cultural Heritage field.
- Compared to laboratory instrumentation it gives the possibility to **quickly scan large, decimetre-scale areas with sub-millimeter spatial resolution.**
- The **polychromaticity** of the synchrotron radiation source gives the possibility to **exploit also other spectroscopic techniques** that like XANES, which complements elemental identification giving **information on their chemical composition.**
- **The artworks must be transported to the facilities.**
- **You need to submit an experimental proposal that can seem complicated at the beginning but becomes simpler with time.**

# TRAINING CAMP

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## Thank you for your attention

Dott.ssa Antonella Balerna



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