

# Ion beam induced luminescence analysis of painting pigments

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## Abstract

Ion beam induced luminescence (IBIL) has been exploited for the first time in the analysis of inorganic painting pigments. The elemental constituents of the different compounds have been determined by particle induced X-ray emission (PIXE). The acquisition time of each spectrum ranges from 100 ms to a few seconds, depending on the luminescence intensity. The luminescence features are fingerprints of the different compounds, thus identifying the provenience of pigments of the same nominal composition. Organic varnish layers do not affect the IBIL features, allowing the identification of pigments, like lapis-lazuli, whose identification with PIXE is hindered by the varnish. IBIL proved to be a technique complementary to PIXE in the archeometry and cultural heritage analysis fields.

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## 1. Introduction

The use of ion beams in the analysis of art objects is mainly linked to the development of particle induced X-ray emission (PIXE). This technique can provide the elemental composition of any kind of material with great sensitivity, from which several information can be inferred on the provenience and manufacturing of art works [1–3].

A challenging application for PIXE is the analysis of painting pigments [4–7]. In fact, the exposure to an ion beam can induce severe damage on the paint layers. In order to minimize the damage, beam currents are kept as low as possible (less than 500 pA). Lowering the current increases the collection time for a single spectrum and, anyway does not always suppress the occurrence of a dark

brownish spot due to the formation in the inorganic matrix of color centers, which can be annealed by thermal, or UV treatments [8,9]. On the other hand, PIXE is unable to determine the composition of organic materials [10] and, moreover, the ion beam heavily damages these compounds leaving irreversible black spots on the surface.

Another problem in the use of PIXE for painting analysis stems from the protective varnish layer, which usually covers the canvas. In fact, this organic coating absorbs low-energy X-rays, hindering the detection of light elements like Na. For example, the analysis of lapis-lazuli ( $3\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{Na}_2\text{S}$ ), which is a precious pigment used in ancient religious art works, relies on other techniques, like PIGE, owing to the high content of sodium [11]. In addition, the damage of the varnish gives rise to the already mentioned formation of unaesthetic black spots.

While numerous spectroscopic techniques have been used in the field of cultural heritage, ion beam induced luminescence (IBIL) has been unexploited until now.

IBIL is the analysis of visible luminescence produced by solid samples during irradiation with energetic charged

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particles. In contrast to processes leading to the production of X-rays, in which the inner atomic shells are involved, the luminescence process is related to the transitions of the outermost electrons involved in chemical bonds of atoms or in network defects. For this reason, IBIL is sensitive to the local chemical environment of compounds and trace substitutes and to the microstructure of the network. The electronic optical transitions are induced by the secondary electrons scattered into the track by the impinging ion. Hence, IBIL as an analytical technique is in principle similar to cathodoluminescence (CL), which is a routinely used for the analysis of minerals and semiconductors [12]. This similarity allows the use of the CL spectra databases for the analysis of IBIL features arising from different compounds.

In the past, Malmqvist and coworkers [13–17] combined IBIL with PIXE in the analysis of geological samples, giving complementary information about the composition and, in some case, exhibiting a better sensitivity to highly luminescent species, like rare earth ions [18]. More recently, IBIL was used for the study of the radiation hardness of organic scintillators [19–21]. In fact, the damage growth during irradiation gives rise to the decrease of the light intensity with a rate depending on the intrinsic radiation hardness of the examined compound.

This paper describes a preliminary work on the use of IBIL for the analysis of inorganic pigments usually employed in paintings. In particular, it is evidenced how IBIL can give spectral fingerprints of different pigments within acquisition times much lower than that needed for the collection of a complete PIXE spectrum. Moreover, the effect of the varnish layer on the IBIL spectrum is discussed, showing it normally does not affect the emission spectrum, especially for materials, like lapis-lazuli, which cannot be analyzed by PIXE when covered by varnish.

## 2. Experimental

PIXE and IBIL measurements were performed with the external microprobe set-up of the AGLAE facility. Detailed description of the equipment can be found elsewhere [22,23]. A 3 MeV proton beam, focused by means of collimators and quadrupole lenses, is extracted to air. The diameter of the extracted beam corresponds to about 50  $\mu\text{m}$  and the current is kept at about 1 nA. The X-rays emitted by the target are collected by two Si(Li) detectors placed at 45° with respect to the beam direction. The first one of thickness 3 mm with an active area of 10 mm<sup>2</sup> and a 0.25  $\mu\text{m}$  BN window, is dedicated to the low-energy range (1–10 keV) corresponding to light elements. The second detector, for the more energetic X-rays (5–30 keV) emitted by heavy elements, is of larger size (thickness 5 mm, active surface 50 mm<sup>2</sup>) with a 6 mm thick Be window and it is placed at 30 mm from the target. A flow of helium along the low-energy detector housing fills all the path between the target and the detector (typically 60 mm) in order to reduce the air attenuation of soft X-rays.

A quartz fiber bundle, connected to a spectrometer equipped with a nitrogen cooled CCD detector, collected the IBIL spectrum in front of the sample. The spectrometer was an Acton 308i, (focal length 300 mm) equipped with a 150 g/mm grating. The CCD (Princeton) is made by 1340  $\times$  100 pixels, 20  $\times$  20  $\mu\text{m}^2$  each one. The use of a CCD for the detection of IBIL spectra allows collecting the full spectrum (from 300 to 780 nm) at once, decreasing the acquisition time. Moreover, the collection with a monochromator, scanning one wavelength at a time, can give spectral distortions induced by the degradation of IBIL intensity during irradiation. Each spectrum was collected by opening the CCD shutter at the beam start for times ranging from 100 ms to 4 s, depending on the emitted light intensity. The wavelength calibration was performed with an Avantes Hg–Ar discharge lamp and the correction factor accounting for the spectral response of the overall detection system (fiber, spectrometer and CCD) was calculated by collecting the spectra of a deuterium and an halogen calibrated lamp (Avantes Cal-HD2000). The correction factor was calculated for giving the correct attribution to the observed spectral features, but in the following paragraphs uncorrected spectra are reported, in order to show the signal-to-noise ratio under the actual experimental conditions.

Fig. 1 shows the beam nozzle, the fiber bundle and the detectors used for collecting the PIXE and IBIL spectra.

The samples were raw minerals or pigment powders available at the AGLAE Laboratory. Pigment powders have been pressed into pellets and part of them has been covered with an organic varnish obtained by an amber based resin. The resin was spread on the samples and dried in air for one day.

## 3. Results and discussion

### 3.1. Pigment analyses

Fig. 2 shows the IBIL spectra of two different lapis-lazuli stones (afterwards indicated as LL1 and LL2), collected with 4 s of acquisition time, corresponding to a total fluence of  $1.2 \times 10^{15}$  ions/cm<sup>2</sup>. As previously stated, lapis-lazuli is hardly detectable by PIXE when a varnish layer is spread on it, since soft X-rays from Na, which is the main constituent of this pigment, are absorbed by the organic coating. So, under these conditions the detection of lapis-lazuli is hindered even at concentrations of 50% in pigment mixtures [11]. From the point of view of IBIL analysis, under irradiation lapis-lazuli exhibits a very intense luminescence, visible to the naked eye, whose spectral shape depends on the examined sample. As can be observed, the signal yield reached after 4 s of acquisition has a high signal-to-noise ratio, evidencing how IBIL can detect lapis-lazuli with an extraordinary sensitivity. In fact, an irradiation of less than 1 s should be enough for collecting a complete spectrum. As will be shown in the next section, the presence of varnish should not interfere with the lapis-

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