Analysis of art objects by means of ion beam induced luminescence

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Abstract. The impact of energetic ions on solid samples gives rise to the emission of visible light owing to the electronic excitation of intrinsic defects or extrinsic impurities. The intensity and position of the emission features provide information on the nature of the luminescence centers and on their chemical environments. This makes ion beam induced luminescence (IBIL) a useful complement to other ion beam analyses, like PIXE, in the cultural heritage field in characterizing the composition and the provenience of art objects. In the present paper, IBIL measurements have been performed on inorganic pigments for underlying the complementary role played by IBIL in the analysis of artistic works. Some blue and red pigment has been presented as case study.

1. Introduction

High energy ion beams are currently employed in several studies of ancient art objects, like manuscripts, jewels, ceramics, metal alloys, paints. In particular, in-air PIXE and micro-PIXE have been widely used owing to the possibility of in situ analysis of art objects of large size or too fragile to be put under vacuum [1]. Since the X-ray production is related to the inner shell electrons, PIXE analysis is quite insensitive to chemical surroundings and valence state of the elements. The visible light created by the ion impact is produced by the outermost atomic electrons, so it yields information about impurities, structural defects and valence states. For this reason, ion beam induced
luminescence (IBIL) may be a complementary analysis technique to PIXE [2,3]. This method is quite similar to cathodoluminescence (CL), but with a deposited energy density orders of magnitude higher. Since CL has been widely used in the analysis of geological samples, the data base available from the CL works can be very useful in the interpretation of the IBIL spectra [4]. In the field of cultural heritage, IBIL can be employed for the identification of materials of similar composition but of different provenience. Moreover, with respect to CL, IBIL measurements can be performed also in air, whereas CL measurements are possible only in vacuum and on coated samples, following procedures which are not always suitable for the analysis of art objects. In this paper, some case study is presented on inorganic pigments where the suitability of IBIL and its complementary role with respect to PIXE is pointed out.

2. Experimental
All the measurements have been performed at the AGLAE Laboratory, at the Centre for Research and Restoration of the Museums of France, located in the Louvre palace in Paris. The fluorescence light is collected by a silica fiber bundle which is connected to an Acton SP-308 optical spectrometer. The light was dispersed by a 150 g/mm grating and focused on a nitrogen cooled Princeton CCD with an 1340x100 pixel array, 20x20 mm each one. The spectrum detection by a CCD allows to reach a high sensitivity and to collect the overall spectrum in the same time, so to avoid spectral distortions due to the emission degradation induced by the ion damage. The spectra have been corrected for the spectral response of the whole detection system (fiber plus spectrometer and CCD detector). The irradiation was performed with a \( \text{H}^+ \) beam of 3.0 MeV with 50 \( \mu \text{m} \) of spot size and a current of about 1 nA. The beam has been extracted in air or helium atmosphere through a nozzle equipped with 100 nm thick Si\( \text{N}_x \) membrane. IBIL spectra have been collected by opening the CCD shutter a second before the irradiation starts for times ranging from 2 to 60 seconds. The analyzed compounds have been blue pigments, like lapis lazuli, azurite and cerulean blue, and red pigments from a color palette from LEFRANC (1933).

3. Results and Discussion
In all the IBIL spectra the plasma lines of the atmosphere surrounding the sample are visible. In Figure 1(a) shows the IBIL spectra of two different kinds of lapis lazuli, whose composition and color are similar. As can be observed, the first one exhibits two main peaks at 450 and 550 nm, with two shoulders at 395 and 625 nm. The second spectrum presents the same peaks, shifted at 460 and 580 nm, respectively, plus an additional peak at about 800 nm. Since lapis lazuli is basically an alumino-silicate material, the peak at 450-460 nm can be related to the intrinsic emission from the silicate structure, as observed in the case of silicate glasses [5]. The intense peak at 550-580 nm can be due to impurities at concentrations beyond the detection limit of PIXE analysis, like Mn\(^{2+}\). Finally, the IR peak in one of the samples can be attributed to Fe related impurities, like Fe\(^{3+}\) or FeS, which are typical impurities of this mineral [6]. In order to evidence the spectroscopic difference with other blue pigments, the IBIL spectrum of cerulean blue is shown in Figure 1(b), exhibiting a faint band at about 650 nm which can be due to CoO excitons [7] or to Co\(^{3+}\) embedded in an oxide structure [8].
Figure 1. (a) IBIL spectra of two different lapis lazuli samples (Na₈Al₆Si₆O₂₄S₄) of the same composition. (b) IBIL spectrum of cerulean blue pigment (CoO*nSnO₂+CoSn(OH)₆). The sharp peaks are the helium plasma lines produced by the ion beam.

Figure 2. (a) IBIL spectrum of an iron oxide based red pigment. (b) IBIL spectra of two red pigments which exhibit the same basic composition by PIXE measurements, i.e. Se, Sr, Cd and Ba.

As far as the red colors are concerned, different kinds of compounds have been identified by means of PIXE measurements. Generally, the IBIL spectra of all the pigments exhibit broad bands in the red part of the spectrum. As an example, in Figure 2(a) is shown the IBIL spectrum of a sample mainly constituted by Fe, as revealed by PIXE, exhibiting a broad feature at about 630 nm. Since Fe³⁺ dispersed in oxide matrices is known to emit at wavelengths higher than 680 nm [9,10], this band can be attributed
to iron oxides like Fe$_2$O$_3$. The attribution is quite sure even if, at present, the CL spectrum of Fe$_2$O$_3$ is not well studied. Only Marshall [5] reports some evidence of red luminescence from hematite. In Figure 2(b) are shown the IBIL spectra of two different colors whose main components, as revealed by PIXE, are Se, Sr, Cd and Ba. Both samples exhibit a very intense band in the IR part of the spectrum, probably related to cadmium compounds like CdTe [11], whose intensity is quite different for the two samples. Moreover, both spectra present a faint shoulder at 600-610 nm indicating the presence of some kind of impurity, like Fe$_2$O$_3$, or to CdS, whose IBIL spectrum exhibits a broad peak in that region [12]. From these examples, that IBIL is a suitable technique for detecting impurities and for evidencing the different structures of samples with the same composition. Moreover, it must be pointed out that all spectra have been collected within a few seconds. These acquisition times allow to minimize the damage effects induced by the ion beam on the art objects. In particular, paintings and organic art objects cannot usually be examined by means of ion beam analysis techniques owing to the coloring effects on the beam spot [13,14].

4. Conclusions
In this paper is presented the suitability in the field of cultural heritage of IBIL, which can be used as a complementary technique with respect to the more conventional ion beam analysis techniques for the identification of inorganic compounds and luminescent impurities.

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