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Towards a portable X-Ray Luminescence instrument for applications in the Cultural Heritage field

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ABSTRACT

Analytical techniques based on luminescence properties of materials have proved to be useful in the study of artistic and archaeological materials. For example iono-luminescence (IL), in conjunction with IBA (Ion Beam Analysis) techniques, and cathodoluminescence (CL), coupled with optical microscopy or SEM (Scanning Electron Microscopy), are important for identifying mineral phases and provenance studies. X-Ray Luminescence (XRL) has been used on Cultural Heritage less than other luminescence techniques; we therefore investigated its potential in this field. The first developed setup, necessarily to be used in the laboratory, was tested on a provenance study of the lapis lazuli "Savoy collection", kept by the Regional Museum of Natural Sciences in Torino. Very interesting results were obtained: while some samples were labelled as Chilean origin (or simply no attribution), XRL spectra clearly excluded that particular provenance for any specimen of the collection.

Although this approach has given valuable information, the potentiality of the technique has not yet been fully exploited due to lack of portability, a great limitation for characterising ancient artefacts. We therefore upgraded the sensitivity of our detection setup, in order to respond also to lower signal levels obtainable with portable X-ray sources. The first results are encouraging and comparable with those obtained with non-portable setups.

INTRODUCTION

The luminescent properties of a material can give useful information about the interpretation of its elemental composition and/or about its structure. Luminescence consists in the emission of photons from the material (usually in the UV-VIS-NIR interval), excited by energy that can be released onto the material itself by different kind of probes (e.g. electrons, ions, photons, heating, etc) [1].

The techniques based on luminescence are widely employed in different fields and especially in the material science characterization [2,3]. Their definition depends on the probe used to induce the luminescence effect: electrons for CathodoLuminescence (CL); ions for IonoLuminescence (IL or Ion Beam Induced Luminescence, IBIL); X-Rays for X-Ray Luminescence (XRL); visible photons for

PhotoLuminescence (PL) and Optical Stimulated Luminescence (OSL); heating for ThermoLuminescence (TL).

In the last decades, many of these techniques found applications also in the Cultural Heritage field: TL and OSL for dating archaeological materials [4,5] while CL, IL and PL for the characterisation of artistic and archaeological materials [6,7]. The best materials to be analysed are stones and gemstones, for which luminescence properties can provide information about their exhaustive characterization and related degree of purity. Furthermore, the method can also highlight the presence of trace elements, quantify phase distribution in rocks, analyse the structure, crystal chemistry (defects, zonal growth, internal structures, trace elements) and microstructural characteristics of minerals/rocks or reconstruct the processes of mineral formation and alteration [8]. Some of these properties, coupled with others, can be useful to trace the provenance of different materials (e.g. jade [9] or lapis lazuli [10]). In gemmology, luminescence was useful in differentiating natural diamond from its synthetic analogues or imitations [11], or to discriminate different gemstones having a great resemblance (e.g. ruby and red spinel). Other natural materials of interest studied by luminescence in the Cultural Heritage field are pearls: freshwater nacre and pearls show a weak luminescence (due to a low Mn^{2+} concentration), whilst nacre, pearls and cultured pearls in saltwater have no luminescence at all (due to lack of Mn^{2+}) [12].

Luminescence techniques require a probe beam impinging on the sample and a photon detector fit for acquiring spectra. The main difference among the various typologies is the analysed volume, both for the spot dimension, depending on the beam diameter, and the probed depth, depending on the kind and energy of the beam. They can be coupled with other techniques using the same probe: for example IBIL can be coupled with the more diffused PIXE (Particle Induced X-ray Emission) and/or PIGE (Particle Induced Gamma-ray Emission) techniques [13]. Depending on the approach used to detect photons, these approaches provide the luminescence spectrum from an analysed point [14], the luminescence map of an area (centred around a specific wavelength or pan-chromatic) [15] or even a combination of them, generating a data-cube containing the luminescence spectrum for each pixel analysed [16]. Another aspect of luminescence developed in these last years that provides useful information is the variation of the signal after a stimulation, obtained thanks to time-resolved luminescence [17,18].

In the Cultural Heritage field, XRL found less application than the other luminescence techniques. Due to this, we decided to possibly 'fill this gap' and investigate its potentialities on some Cultural Heritage materials, taking into account its peculiarities and differences with respect to the other techniques. CL requires operating in vacuum and allows for the analysis of relatively small samples, considerably limiting its applicability in the considered field [19]. Conversely, IL can be carried out in air and samples of almost any shape and dimensions can be analysed but it requires a particle accelerator. In addition, only movable objects can be analysed – a factor that severely limits the safety and conservation issues related to the handling of an artwork or archaeological find from a museum to a laboratory [20]. PL overcomes this problem thanks to its portability [21], but in our opinion XRL has the great advantage that it can be coupled to X-Ray Fluorescence (XRF), a widespread technique with many applications in the Cultural Heritage field. In fact XRF, thanks to the diffusion of both benchtop and hand-held instruments, has been applied on many and different materials [22-24], allowing the analysis of many samples in a very short time [25].

The first XRL setup we developed had necessarily to be used in the laboratory; we tested its applicability to the Cultural Heritage field trying to perform a XRL provenance study on lapis lazuli – the further step of an investigation carried out since 2007, by using a multi-analytical approach [19]. Lapis lazuli is a beautiful rock, an aggregate of several different minerals (mainly lazurite, calcite and pyrite); it has been widely employed since the antiquity by many civilisations, from the Indus Valley

to Egypt [10]. We studied it both in terms of composition [26] and luminescence properties [20], with the final aim to develop a protocol able to differentiate the materials coming from four different possible provenances. This protocol was successfully applied both to artistic [20] and archaeological materials [10]. For this latter XRL study, only the luminescence properties of the material were taken into account: the main marker allowing for the discrimination of the lapis lazuli from Chile is the presence of wollastonite (CaSiO_3). This phase, in fact, does not occur as a minor mineral in any of the other Asian provenances. Wollastonite has a very strong luminescent emission if compared to all the others minerals present in lapis lazuli, showing two main bands centred at around 560 and 620 nm. On the other hand, the Asiatic samples, in which the dominant luminescence is due to diopside ($\text{CaMgSi}_2\text{O}_6$), show a typical band at 585 nm. In addition, both minerals (wollastonite and diopside) also show an emission centred at 450 nm, due to the siliceous matrix – not useful for provenance purposes. After having analysed several samples of known provenances and having thus created a luminescence database for lapis lazuli, we managed to study some specimens from the “Savoy collection”, kept by the Regional Museum of Natural Sciences in Torino (Italy). The related results are exhaustively detailed below.

Although this approach has actually given valuable information, the potentiality of the technique has not yet been fully exploited due to lack of portability, a great limitation for the characterisation of valuable and ancient artefacts. Therefore we managed to upgrade the detection setup in order for it to be sensitive also to lower signal levels, obtainable with portable X-ray sources.

EXPERIMENTAL SETUP

The first setup we developed to acquire XRL spectra is not portable and has to be operated in a shielded area for radioprotection issues. The employed X-Ray source is part of an instrument developed to acquire radiographies and tomographies on Cultural Heritage materials [27-29]: it is a General Electric ERESKO MF4 with a tungsten anode, operated with a voltage and current suitable to maximise the XRL signal. The UV-VIS-NIR photons, induced by X-rays in the samples under analysis, are collected through a modified Ocean Optics ISP-REF integrating sphere and led to the spectrometer through a 1 meter long optical fiber (600 μm diameter). The spectrometer is an Ocean Optics USB4000 – the same we already used for ionoluminescence measurements [20]: its detector has 3648 pixels, it is fitted with a 600 l/mm grating blazed at 500 nm and its maximum integration time is 65 seconds. For XRL measurements, the spectrometer has been placed behind a lead shielding, thus avoiding the risk of being hit by scattered X-rays.

The second setup we developed, shown in Figure 1, was intended to simulate a typical portable-XRF condition. The X-ray source is a Microfocus Hamamatsu L8121-03, equipped with a tungsten anode and generating a cone beam usually exploited to perform micro-radiographies and tomographies. To narrow the X-ray cone to a spot, we realised a 1 mm thick lead collimator with a hole of 8 mm diameter; the source is operated with a 40 kV voltage and a 500 μA current. The light generated by the investigated sample is collected through an Ocean Optics 74-UV collimating lens, placed at an angle of about 105° with respect to the beam direction – the maximum achievable value in order to minimise the distance from the sample. The lens is linked to an Ocean Optics QE Pro spectrometer through the same optical fibre of the previous setup. This spectrometer allows for low-level light detection thanks to a TE-cooled detector – namely a Hamamatsu S7031-1006S FTT-CCD detector, with a 2D arrangement of pixels (1044×64). The selected grating is blazed at 400 nm and the analysable range is from 250 nm to 630 nm, thus having a high sensitivity also in the UV region. Also this spectrometer is adequately shielded, together with an Ocean Optics DH-mini lamp connectable

to the same optical fibre and used to recognize the acquisition spot on the sample. A camera frames the sample and helps in evaluating the area to be analysed.

During the acquisition of all XRL spectra, lights have been switched-off in order to minimize the environmental background signal. From all the measured spectra presented in this paper, the dark signal was subtracted and the results corrected for the spectral response of the instrument.

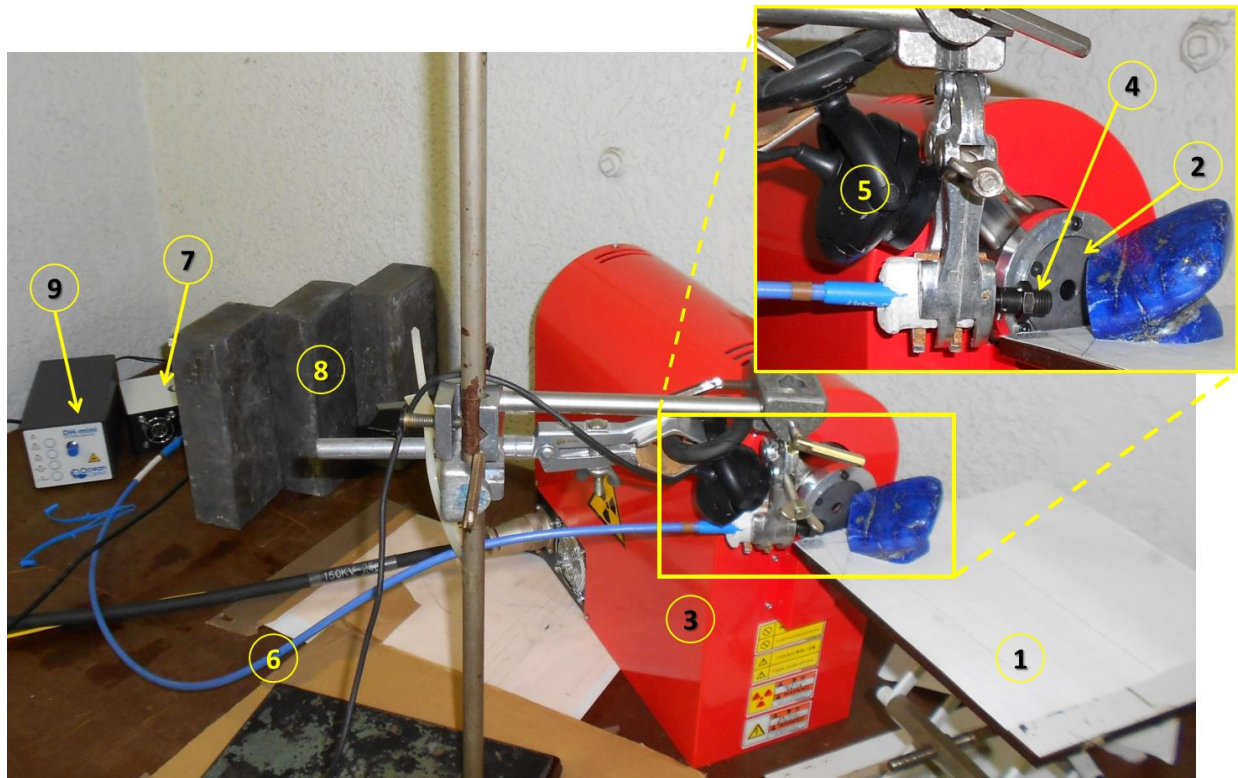


Figure 1: the XRL apparatus assembled to simulate p-XRF conditions. Numbers refer to: (1) lab-jack to place and move the sample; (2) lead collimator; (3) X-ray source; (4) collecting lens; (5) camera; (6) optical fiber; (7) spectrometer; (8) lead shielding; (9) lamp.

THE ANALYSED SAMPLES

Lapis lazuli stones and related semi-thin sections, used to check the applicability and reliability of the conceived portable XRL apparatus, are those already analysed in a previous work and there exhaustively described [10]. To obtain statistically significant results several areas have been analysed for each sample, but since it is not the focus of this paper, in the following only one spectrum for two of the main provenances are reported.

In addition, five lapis lazuli samples belonging to the 19th century “Savoy Collection” of the Regional Museum of Natural Science (Torino, Italy) were also investigated. This collection is composed of rock samples, decorative elements and polished items having no definite information, except for some unchecked detail described in the museum catalogue. These objects are shown, together with their representative pictures, in Table 1. Further general information about the mineralogical collections of the museum is reported in the volume [30].

Table 1: Main features of the analysed samples; in the last line, the attribution executed by Trossarelli and Peyronel, as appearing in the museum catalogue, is reported for some of the samples.

**“Savoy Collection”
of the Regional Museum
of Natural Science
(Torino)**



Catalogue number	<i>M/U6565.1</i>	<i>M/U6565.2</i>	<i>M/U6565.3</i>	<i>M/U15601</i>	<i>M/U15602</i>
Dimensions (cm)	4 × 4 × 0.2	3 × 3 × 0.3	1,5 × 1 × 1	4 × 3.5 × 0.3	4 × 3.5 × 0.3
Description	polished lapis lazuli; small circular plate	polished lapis lazuli; small rectangular plate	fragment	polished lapis lazuli; fragment of a plate	polished lapis lazuli; fragment of a plate
Provenance (catalogue)	-----	-----	-----	-----	-----
Attribution [Trossarelli and Peyronel]	Chile	Chile	Chile	-----	-----

RESULTS

To test the potentiality of XRL and evaluate its applicability to samples of different shape and dimensions, various setups and conditions have been tested. The first step has been to verify the presence of a XRL signal from lapis lazuli that was comparable to the one already obtained with other luminescence techniques (i.e. CL and IBIL). For this purpose, we selected some of the semi-thin sections that had been already analysed in previous works [10] and put them directly in contact with the integrating sphere, placing the sample the closest as possible to the focal spot of the X-ray tube. It is worth noticing that, in this configuration, the analysed area corresponds to the hole of the integrating sphere (diameter of 10.32 mm). The CL and IBIL measurements we performed in the past were obtained from single crystals of a specific mineral phase, with maximum dimensions in the order of some hundreds of microns. With this XRL setup, a very large area (if compared to the grain size of lapis lazuli crystals) is analysed instead, so that the mean luminescence spectrum from several different crystals is acquired. In lapis lazuli, two distinct mineral phases show very intense luminescence spectra (if compared to all the others): wollastonite (typical of Chilean samples) and diopside (typical of an Asian provenance). The spectra of these two minerals remain the dominant ones also when analysing large areas of the sample, containing other mineral phases – as in the tested experimental setup. Two examples of spectra are shown in Figure 2a; the related setup parameters are reported in Table 2. If compared to CL and IBIL spectra [19], acquired on single crystals, the results are unequivocally comparable: the luminescence bands remain the same and – consequently – a discrimination among different provenances of the specimens can be thoroughly achieved.

Although these results are encouraging, this method can hardly find feasible applications in the Cultural Heritage field, as it requires thin and small samples to be probed – two very limiting factors, in an area of study where the use of non-invasive and non-destructive approaches is of fundamental importance. Due to this, we tried to directly analyse lapis lazuli rocks using a different XRL geometry: the sample was put directly in contact with the integrating sphere and this latter was positioned close to the focal spot of the X-ray tube. By using this setup, the tube-generated X-rays were allowed to pass through the integrating-sphere cavity, hitting the sample on the other side. This particular geometry causes the sample to be farther from the X-ray source – so that the luminescence signal is necessarily lower – but it allows the direct analysis of specimens of different shape and dimensions. Two of the collected spectra are shown in Figure 2b: notice that, although the recorded signals are lower than the previous ones, the main features allowing the discrimination among different lapis lazuli provenances are still clearly detectable.

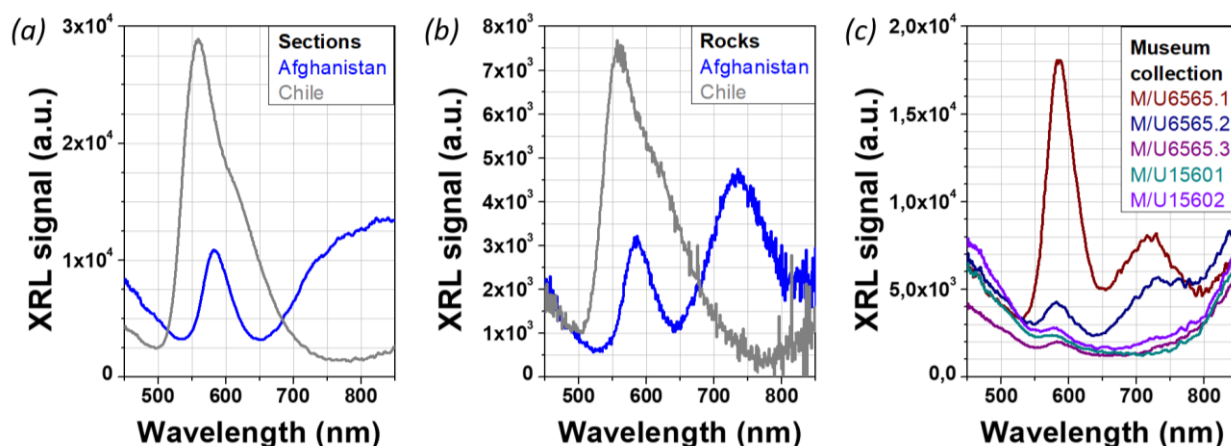


Figure 2: XRL spectra of lapis lazuli acquired with different setups (see Table 2 for more details):
 a: semi-thin sections (different integration times have been used for Chilean and Afghan samples); b: rocks; c: samples from the Museum Collection.

Table 2: details of the parameters and experimental setups used to acquire the XRL spectra; for semi-thin sections different integration times have been used for Chilean (C) and Afghan (A) samples.

Samples analysed	semi-thin sections	rocks	museum collection	rocks
Tube voltage (kV)	90	90	150	40
Tube current (mA)	10	10	6	0,5
Position of the light collector	behind the sample	same side of the beam	behind the sample	same side of the beam
Spectrometer	OO USB4000	OO USB4000	OO USB4000	OO QEPro
Integration time (s)	10 (C) / 65 (A)	65	65	180
number of averaged spectra	3	5	3	1
Total acquisition time (s)	30 (C) / 195 (A)	325	195	180

Being confident about the fact that these results could be extended to objects of interest in the Cultural Heritage field, we further optimized this method of data collection applying it on five selected lapis lazuli samples of the “Savoy Collection” of the Regional Museum of Natural Science in Torino, specifically brought to our laboratory for provenance determination. Due to the small dimensions of the samples, the same geometry employed for the semi-thin sections was adopted. As the thickness of these objects is significant (with consequent higher X-ray absorption), we increased the X-ray tube voltage up to 150 kV. The results are shown in Figure 2c: all the acquired spectra are characterised by a band centred at 585 nm, which is typical of the lapis lazuli from Asia. Moreover, samples M/U 6565.1 and M/U 6565.2 show also a second band around 725 nm, which can help for a future more precise attribution of these samples. The Chilean attribution, previously hypothesized for some of these samples, has therefore to be excluded. Despite its small statistics, such an achievement represents a very important result because it demonstrates the possibility to apply XRL directly to Cultural Heritage objects – without preliminary treatment – and to discriminate very quickly the provenance of lapis lazuli materials from museum collections.

The last missing step in order to render this technique fully applicable to the Cultural Heritage field is the portability, which is necessary for all those artworks and archaeological objects that cannot be moved from their museums. To overcome this limitation, we had to totally change the setup: the

X-ray source employed for all the previous measurement, in fact, cannot be easily moved in museums – both for its weight and for size, but especially because of radioprotection limitations. To perform some feasibility tests, we then decided to use a smaller X-ray tube and to run it in conditions typical for a portable XRF apparatus (40 kV and 500 μ A). By using this X-ray beam, no luminescence signal can be detected with the spectrometer employed for the previous measurements. A new spectrometer, equipped with a cooled detector, was therefore acquired. Furthermore, the geometry of acquisition has also been modified, by excluding the integrating sphere and using a collecting lens, in order to maximize the signal and minimize the distances between source, sample and detector. The final setup resulting after these tests is shown in figure 1; the related experimental details are reported in the last column of Table 2. By using this configuration, an integration time of 3 minutes is more than enough to obtain a good enough quality for luminescence spectra, which allow for the discrimination of the lapis lazuli provenance, as clearly shown in Figure 3.

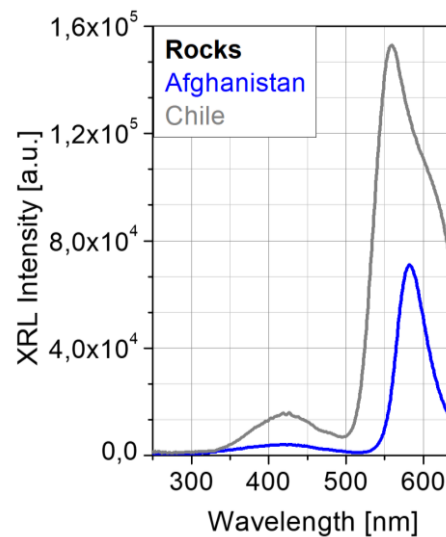


Figure 3: XRL spectra of lapis lazuli rocks from two different provenances excited by a p-XRF equivalent X-ray tube and detected with a cooled spectrometer (see Table 2 for more details).

CONCLUSIONS

The applicability of XRL to the Cultural Heritage field has been investigated. Different non-portable setups have been tested and optimized in order to verify the possibility to discriminate the provenance of lapis lazuli using XRL, obtaining satisfactory results both on semi-thin sections and on rocks. The developed method has been successfully applied to study the provenance of five samples of the “Savoy Collection” kept at the Regional Museum of Natural Science in Torino, excluding the Chilean provenance (attributed on the basis of previous descriptions) for any of the analysed samples.

To further study the applicability of this technique, a new setup based on a cooled spectrometer has been developed and tested, using an X-ray source run in conditions typical of p-XRF setups. The obtained results are comparable to the previous ones, thus demonstrating the possibility to use this technique in a portable way and to apply it also in museums or archaeological excavations.

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