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New approaches for investigating paintings by ion beam techniques

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ABSTRACT

Up to now, among the IBA techniques, only PIXE has been used for analyzing paintings. However, quantitative PIXE analysis is sometimes difficult to interpret due to the layered structure, the presence of varnish and organic binder and, in some cases, discoloration of the pigments has been observed due to the interaction of the ion beam with the compounds.

In order to improve the characterization of paintings, we propose some alternative experimental procedures. First of all, backscattering spectrometry (BS) and PIXE are simultaneously combined in order to collect complementary information such as layer thickness and organic compound quantification. The simultaneous PIXE and BS experiments also have the advantage of being able to analyze the same area in one experiment. This combination, implemented with an external beam, was directly applied on paintings and on painting cross-sections for the study of Italian Renaissance masterpieces. We have obtained valuable results not only on the pigment itself but also, for the first time, on the binder to pigment proportion which is not well documented in the ancient recipes. Moreover, in order to restrain beam damages due to the ion stopping power, we propose to analyze very thin painting cross-sections by a combination of PIXE–RBS and Scanning Transmission Ion Microscopy (STIM).

1. Introduction

Particle Induced X-ray Emission (PIXE) has been used for the last decade for painting analysis [1–6]. This technique, well adapted to the detection of the elements heavier than sodium, has given successful results for the characterization of pigments based on mineral compounds [7,8]. However, organic pigments as well as binders or varnishes cannot be identified by X-ray based techniques.

In order to analyze the organic components of the paintings, other independent techniques such as Fourier Transform Infrared Spectrometry (FT-IR) [9], gas chromatography (GC) [10] and related methods (mass spectrometry GC/MS, pyrolysis PyGC, and High Performance Liquid Chromatography HPLC [11]) have to be carried out. Up to now and for specific cases, only infrared and Raman spectroscopies are able to analyze both organic and mineral matrices [12].

PIXE is also known for its limited depth resolution but many efforts have been undertaken to analyze the stratigraphy of the paint layers. Differential PIXE, based either on the variation of the particle energy [5,6,13] or on the variation of the target angle [14] and more recently of the detection angle [15], is one of the possibilities to access at different analyzed depths. The other choice is based on the X-ray spectrum itself by using the intensity ratios of K/L or L/M X-rays for measuring the position of an element in layers [16]. Differential PIXE is very efficient but also time consuming because the experiment has to be repeated with different projectile energies (or at different angles).

In order to collect the most complete possible information on paintings, we propose some alternative IBA experimental procedures including simultaneous RBS and PIXE, STIM and mono-energetic X-radiography by using X-ray emission induced by particles. In this paper, due to the limited number of pages, we focus on the development of simultaneous backscattering spectrometry (BS) and PIXE directly applied on paintings or on painting cross-sections. The advanced main information of the BS with regard to PIXE is the determination of the thickness and pigment-to-binder proportion. The combination of PIXE and BS was applied to the study of Italian Renaissance masterpieces.

A first experiment on a combination of PIXE–RBS and Scanning Transmission Ion Microscopy (STIM) on very thin painting cross-sections is also presented.

2. Paintings samples

Different samples of painting have been arranged. A first set of samples (A) has been prepared by mixing different known ratios of

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pure white pigments (lead white, zinc white, titanium white, gypsum, calcite) and binder (linseed oil or animal glue). The second sample is a painting (B) prepared by a restorer according to the traditional recipes of the 15th–16th centuries for the realisation of flesh tones. The painting is composed of *gesso* layer, a mixture of gypsum and animal glue, laid on a wood support as a preparation layer. Various layers of lead white with or without red pigment (vermilion or iron oxide) mixed with linseed oil are applied on the *gesso* substrate. In some parts of the painting a thin layer of glaze (rich in linseed oil, with low manganese content) was added for modeling shadows in the flesh tones. The analyses were carried out directly on the painting as well as on the cross-section of micro-samples (typically less than 1 mm^2). Thick conventional (Bcs1) and thin transversal (Bcs2) cross-sections prepared with a microtome [17] were examined.

Painting cross-sections from Italian masterpieces of the 15th–16th centuries (samples C) were selected for the determination of the pigment-to-binder proportion.

Table 1
Lead white layer thickness (μm) measured by Scanning Electron Microscopy (SEM) and BS.

Sample	SEM (minimum–maximum)	BS
A1	0–13	1–4
A2	15–38	25–32
A3	48–71	>40

3. Experimental conditions

3.1. Simultaneous PIXE–RBS

A 3 MeV-proton beam has been selected in order to analyze light and heavy elements in the paintings [18]. Medium to high-Z major, minor and trace elements are measured by PIXE. Backscattering spectrometry (BS) is used for detecting low to high-Z major elements. In particular, due to the intense non-Rutherford

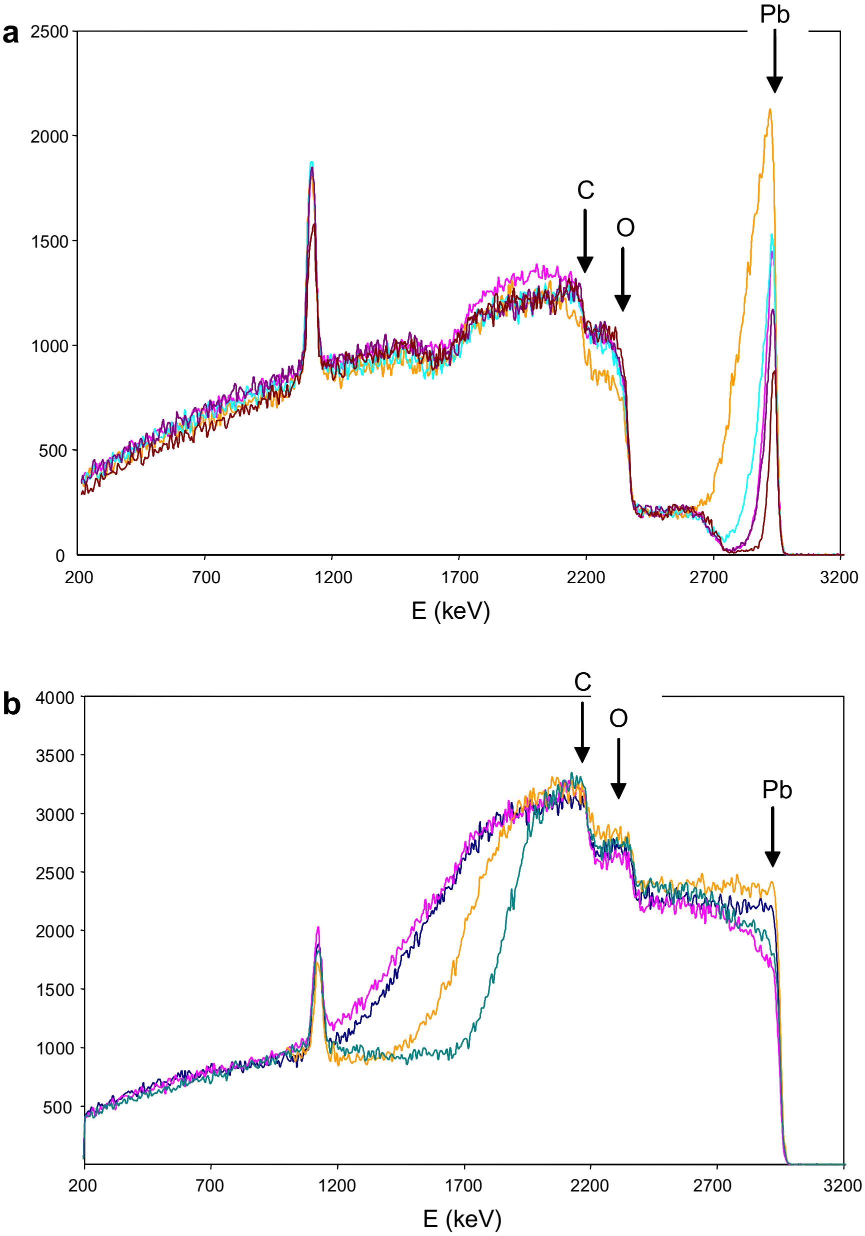


Fig. 1. BS spectra of sample B. Lead white (basic lead sulphate) – thin (a) or thick (b) layer-on *gesso* (gypsum). Experimental conditions: H$^+$, 3 MeV, $\theta = 45°$, $I \approx 1$ nA, Q = 0.3 μC, beam diameter ≈20 μm.

cross-sections for low-Z elements, 3 MeV-protons are well adapted to the analysis of C and O which are of great interest for the quantification of the organic ingredients of the paint. Furthermore, the simultaneous operation of PIXE and BS presents the advantages of analyzing the same area in one experiment reducing experimental time and potential discoloration of the pigments [19–21].

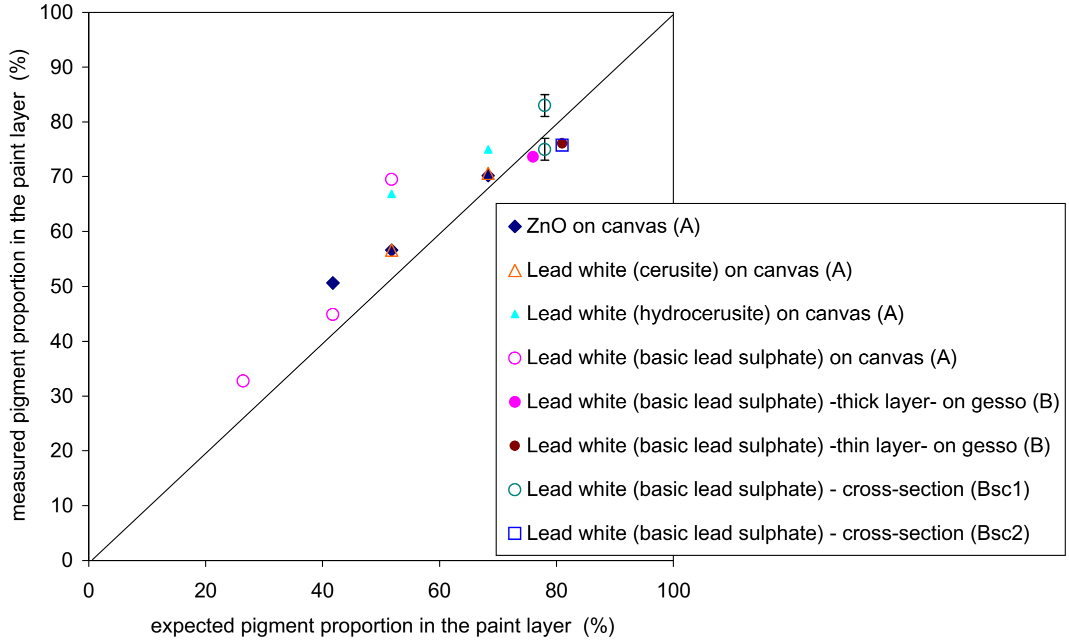
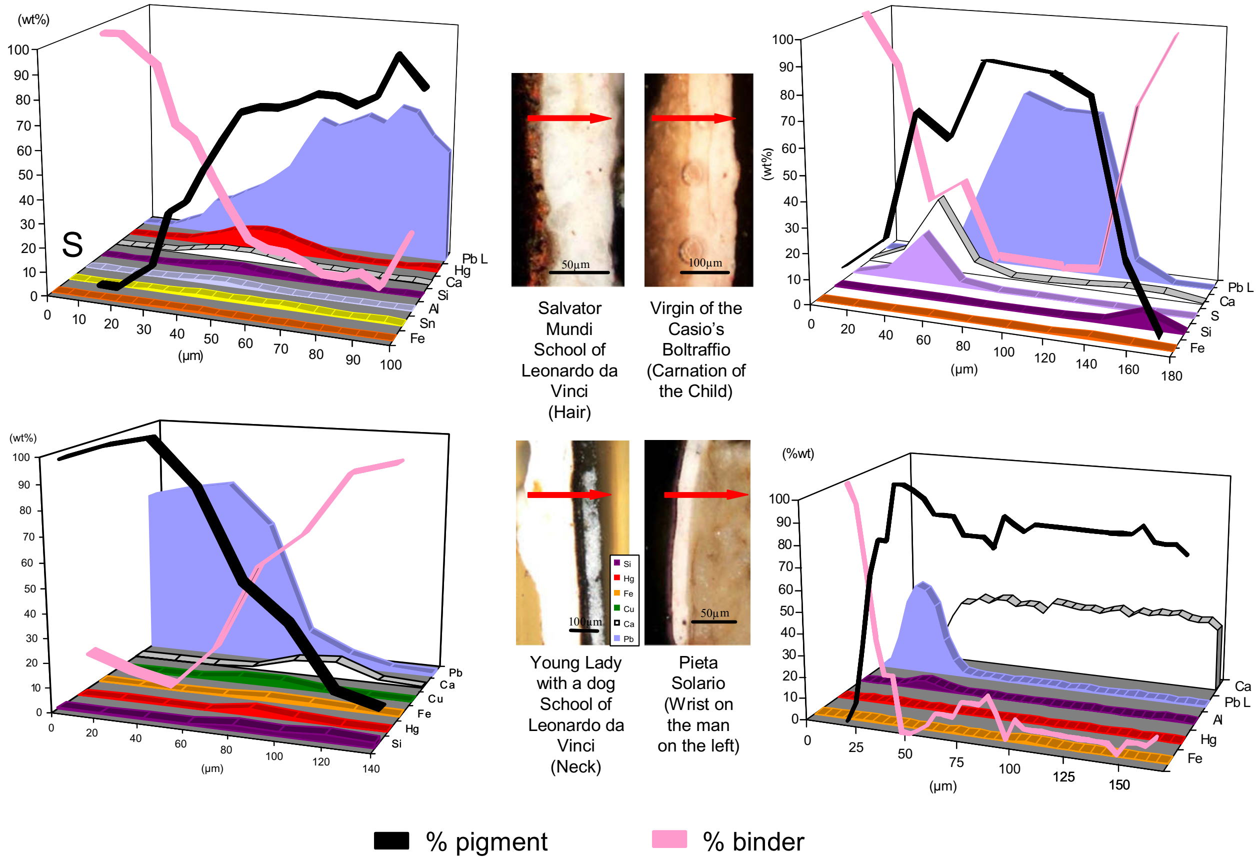


Fig. 2. Comparison between measured and expected pigment content in paint layers containing various amount of pigment and linseed oil.


Salvator Mundi School of Leonardo da Vinci (Hair)

Virgin of the Casio's Boltraffio (Carnation of the Child)

Young Lady with a dog School of Leonardo da Vinci (Neck)

Pieta Solario (Wrist on the man on the left)

Fig. 3. Elemental profiles along painting cross-sections of Italian Renaissance masterpieces determined by the combination of PIXE and RBS. Total pigment and binder contents are also reported.

Paintings and thick cross-section samples (A, B, Bcs1 and C) were analyzed by the external proton beam of AGLAE (Centre de Recherche et de Restauration des Musées de France-C2RMF) [22]. The external beam set-up allows one to perform PIXE, PIGE and BS simultaneously with two Si(Li) X-ray detectors at 45°, one HPGe γ-ray detector and one Si surface barrier detector placed at 150° [23]. For monitoring the beam, the dose is measured by a Peltier-cooled X-ray detector on the Si–K peak emitted by the Si_3N_4 exit window. More recently, the dose measurement is achieved by deflecting the beam to a gold foil located in the exit nozzle; the backscattered particles are counted by an annular surface barrier detector [24]. The beam diameter was 40 μm for the painting and about 20 μm for the cross-section analysis.

Thin cross-section samples (Bcs2) were analyzed at the AIFIRA platform (Centre d'études nucléaires de Bordeaux-Gradignan – CENBG, France). This recently developed ion beam facility is equipped with a 3.5 MV singletron DC positive ion accelerator. The RBS measurements were performed using a Si surface barrier detector placed at 135° from the incident proton beam direction of 3 MeV. X-ray emission measurements were made with a Si(Li) energy dispersive detector, placed at a 45° angle on the beam axis, and using a 325 μm thick carbon filter.

PIXE spectra have been fitted by GUPIX or GUPIXWIN [25], which extract elemental concentrations of the mineral compounds. BS spectra have been simulated with SIMNRA [26] for both Rutherford and non-Rutherford parts of the spectra. Self-consistent automated PIXE–RBS depth profiling using PIXE spectra and BS has been also tested [27]. A PIXE–RBS mapping system has been recently developed at C2RMF [28].

3.2. Scanning Transmission Ion Microscopy

STIM was carried out at AIFIRA using a 3 MeV alpha beam in order to improve energy loss contrast on such thin specimens. The beam diameter is 3 μm and a very low beam intensity of about 1000 ions/s was achieved. The residual energy after passing through the sample was measured in a passivated implanted planar silicon detector (Canberra PIPS detector, 100 mm^2, 16 keV resolution), placed at 0° on the beam axis. The energy of transmitted ions and the corresponding position of the beam were stored in append mode in a binary data file in order to carry out off-line data reduction.

4. Results

4.1. Simultaneous PIXE–RBS on paintings and thick cross-sections

The mineral matrix composition, giving access to the mineral pigment and extender concentrations, is calculated from the low-energy X-ray spectrum. Trace elements can be measured from the high-energy X-ray spectrum. Carbon and oxygen contents are extracted from the BS signal which also includes the major higher Z elements. Hydrogen is adjusted in the BS spectrum simulation. By taking into account the C and O contents originating from the pigments, it is possible to calculate the carbon and oxygen contribution of the binder. Details of the calculation procedure can be found in [18,29]. As a result, we obtain the full characterization of the paint layers: concentration in pigments and extenders, binder to pigment proportion and thickness.

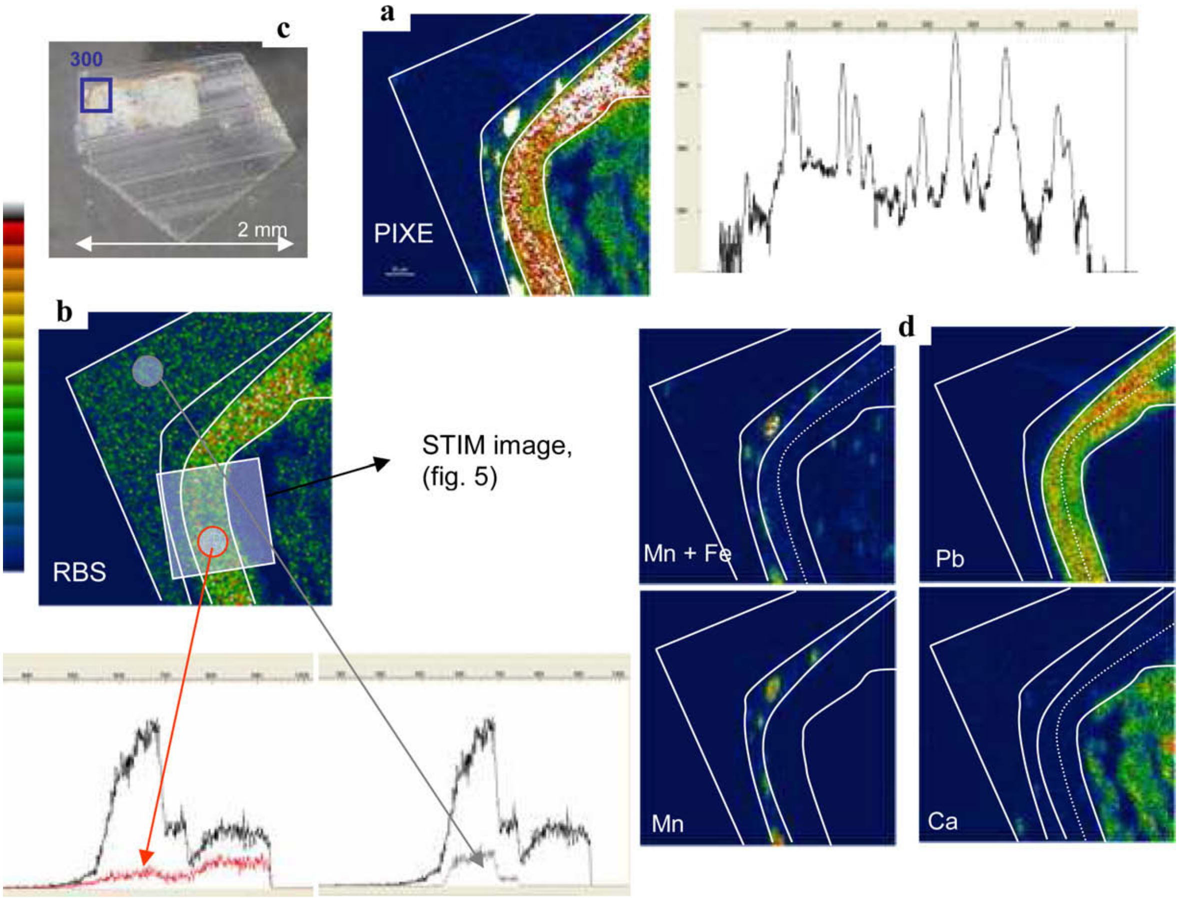
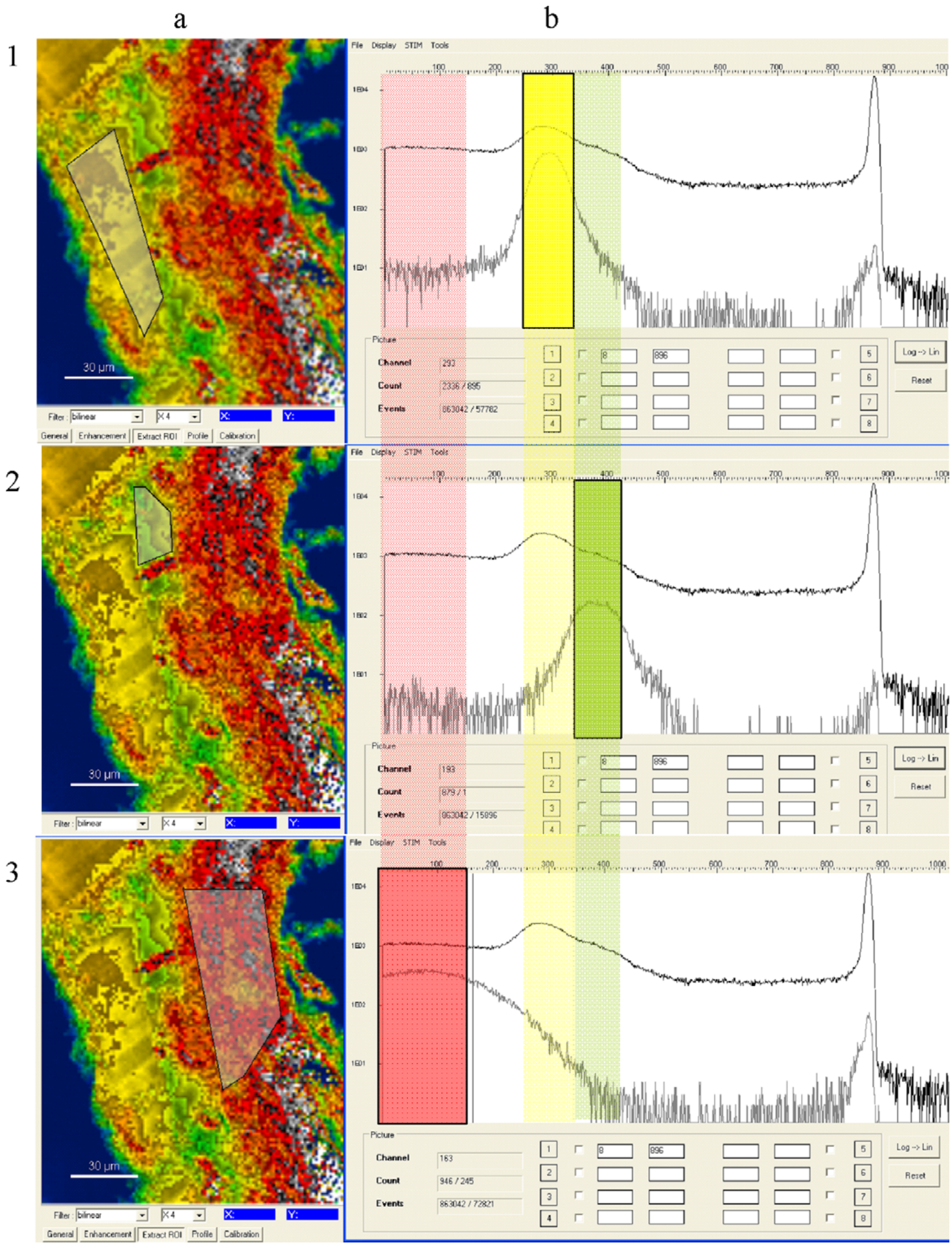


Fig. 4. PIXE (a) and RBS (b) mapping of painting thin cross-section (c). Experimental conditions: H$^+$, 3 MeV, beam diameter ≈2 μm. Elemental maps (d) clearly show the layered structure of the painting sample: the *gesso* layer containing Ca and some grains of Fe, one lead white layer covered by a lead white layer containing trace of Fe and then the glaze layer including Mn grains.

Thick layers of lead (A and B) or zinc white (A) have been investigated by simultaneous PIXE and BS. BS spectra are presented in Fig. 1. Layer thickness has been calculated by using SIMNRA or by the surface energy approximation [30]. The thickness was also directly measured on the cross-section by SEM for comparison (Table 1). Slight discrepancies are mainly due to the irregularity of the layers and to the different probe size.

The proportion of pigment to linseed oil has been calculated from the Pb/Zn, O, C and H atom concentrations (Fig. 2). The measured results are in close agreement with the expected values. A slight excess in measured pigment is due to a partial absorption of the oil by the canvas. This behaviour is not observed when the lead white layer is laid on a preparation layer (*gesso*).

When the layers are too thick or too numerous, it becomes difficult to extract accurate information from the BS spectrum. So, for the determination of the binder to pigment proportion of Italian Renaissance masterpieces (15th–16th centuries), we analyzed painting cross-section samples (C) from the C2RMF laboratory collection. These small painting samples were taken during past restoration and embedded in resin. The same procedure developed for the direct analysis of paintings has been applied for the samples. Profiles are presented in Fig. 3. The concentrations of



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1:
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Count 2336 / 895
Events 863042 / 57762
8
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2:
Channel 193
Count 879 / 1
Events 863042 / 15896
8
896

3:
Channel 163
Count 946 / 245
Events 863042 / 72821
8
896

Fig. 5. STIM image (a) and spectrum (b) of painting thin cross-section. 1: embedded resin layer. 2: glaze layer. 3: lead white layer.

elements in the pigment and the proportions of pigment and binder are reported.

These results are quite homogeneous: when the pigment is not mixed with other coloured pigments, the proportion of lead white is from 85 to 95 wt% for a binder content of 15–5 wt%.

For coloured layers containing other pigments, such as vermillion (e.g. painting 'Salvator Mundi'), the binder content is 35%, whereas it is around 15% in the adjoining layer containing only lead white. These observations are directly comparable to the oil absorption value of each pigment. The oil absorption value is the minimum amount of linseed oil which must be added to a pigment to transform it from a powder to a cohesive plastic mass. This value is around 8% in weight for lead white and higher for vermillion and umber [31]. The average of 10% measured on the paintings of the Italian Renaissance is clearly in agreement with this value and with the advice given in the Marciana manuscript of the 16th century: "Grind up the colour (...) with as little oil as possible" [32]. This text, which was the only one found in several books of recipes about the proportion of pigment-binder, clearly refers to a very small amount of oil, which corresponds to the modern definition of the oil absorption value.

4.2. Simultaneous PIXE–RBS and STIM on thin cross-sections

Thin samples (Bcs2) of 10–15 μm thick have been chosen as the most appropriate thickness for STIM. Simultaneous PIXE–RBS maps have been carried out on a larger area of the same sample (Fig. 4). Elemental maps clearly show the layered structure of the painting sample: the *gesso* layer containing Ca and some grains of Fe, one lead white layer covered by a lead white layer containing trace of Fe and then the glaze layer including Mn grains. BS spectra of the lead white layer were extracted in order to determine the pigment-to-binder proportion (reported on Fig. 2). The STIM data is presented in Fig. 5. The transmission particle spectrum is sensitive enough to distinguish the glaze layer from the embedded resin. This first STIM experiment on paintings is promising for the characterization of multilayers of varnish, glaze and organic pigments.

The capacity of distinguishing mutilayer structure – preparation layer/lead white/reddish layer for flesh tones/glaze for shadows is really interesting for a better understanding of the *sfumato*. This technique, under study in the laboratory [33], was used by Leonardo da Vinci and his followers for making subtle gradations, without lines or borders, from light to dark areas.

4. Conclusion

The combination of PIXE and BS is successful for the characterization of painting layers. PIXE gives access to the elemental composition (major elements to traces) of the mineral compounds, pigments and extender. BS provides the thickness information and the organic compound estimation. The simultaneous PIXE and BS experiments have the advantage of being able to analyze the same area in one experiment, limiting experimental time and beam damage. The data treatment is handy by using routinely available simulation softwares.

The PIXE–RBS results provide advanced information on the pigment-to-binder proportion of Italian Renaissance paintings. These results are useful because this parameter is not well documented in the ancient recipes and is very important for the understanding of the paint rheological properties [34]. STIM seems to be promising for the characterization of varnish, glaze and organic pigments.

Acknowledgments

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