

## Characterization of white pigments and paint layers by simultaneous PIXE and Backscattering Spectrometry

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**Abstract.** PIXE is now routinely used for analyzing paint layers. Various set up have been developed to investigate the elemental composition of samples or wood/canvas paintings. However, quantitative PIXE analysis is sometimes difficult to interpret due to the layered structure, the presence of varnish and organic binder. Backscattering spectrometry (BS) can be a useful complementary method to overcome these limitations. By using 3 MeV protons for PIXE and BS simultaneously, it was possible to perform quantitative analysis including C and O for which the non-Rutherford cross sections are intense. Furthermore, by using the same conditions for PIXE and BS, the experiment time and the potential damage by the ion beam were reduced. The results obtained with the external beam of AGLAE on a large set of pure white pigments (lead white, basic lead sulphate, calcium sulphate, gypsum, calcite, zinc oxide, titanium oxide) and on various mixing ratios of pigment and linseed oil are shown. Simultaneous combination of PIXE and BS leads to a complete characterization of the paint layers: elemental composition, thickness, varnish layer thickness and proportion of the organic binder have been determined.

**Keywords:** PIXE, RBS, paint layers, white pigments

### INTRODUCTION

Particle Induced X-ray Emission (PIXE) has been used in the last decade for the analysis of paintings<sup>1,2,3,4,5</sup>. This technique gives access to the detection of the elements heavier than sodium, up to uranium. Consequently, only mineral compounds can be identified and quantified whereas the organic part of the painting is neglected. In order to analyze the organic compounds, other independent techniques, such as Fourier Transform Infrared Spectrometry (FT-IR)<sup>6</sup>, gas chromatography (GC)<sup>7</sup> and related methods (mass spectrometry GC/MS, pyrolysis PyGC, and High Performance Liquid Chromatography HPLC<sup>8</sup>) have to be carried out.

Up to now and for specific cases, only infrared and Raman<sup>9</sup> spectrometries are able to analyze both organic and mineral matter.

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<sup>10</sup> (see also for example N. Grassi *et al.* or Z. Smit *et al.* in this conference) or on the variation of the target angle<sup>11</sup> and more recently of the detection angle<sup>12</sup>, 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<sup>13</sup>.

Differential PIXE is very efficient but also time consuming because the experiment has to be repeated with different projectile energies (or at different angles). For many reasons, after-specified in this paper, simultaneous Backscattering Spectrometry (BS)

has been chosen to complement PIXE for the characterization of paint layers.

## **SIMULTANEOUS PIXE AND BS**

For paint layers as well as for paintings, the expected advantages of using simultaneously PIXE and BS are the following:

- same analyzed area
- one experiment: short experimental time
- basic data treatment
- less damage
- complementary results

## **Samples and Experimental Conditions**

Samples of paint have been prepared by mixing different ratios of pigment and binder. Every paint was constituted by a mixture of microscopic pigment particles mixed in linseed oil that holds the pigment in suspension, allows it to be applied with a brush, and then dries to bind it to the support (canvas). Pure white pigments (lead white, basic lead sulphate, calcium sulphate, gypsum, calcite, zinc oxide, titanium oxide) were also prepared in pellets for comparison. Samples were analyzed by the external proton beam of AGLAE (Centre de Recherche et de Restauration des Musées de France-C2RMF)<sup>14</sup>. The external beam set-up<sup>15</sup> allows to perform simultaneously PIXE, PIGE and BS with two Si(Li) X-ray detectors, one HPGe  $\gamma$ -ray detector and one charged particle detector. A Peltier-cooled X-ray detector is used for monitoring the beam dose using the Si-K peak emitted by the exit window. A 3 MeV-proton beam has been selected for the experiments. Despite its poor discrimination for heavy elements, BS with protons has some interesting characteristics, specially a large analyzed depth in the material and intense non-Rutherford cross-sections for low Z elements. Advantages associated with the use of 3 MeV protons (Table 1) have allowed us to analyze thick layers and to increase the sensitivity for the detection of C and O which can partially be attributed to the organic ingredients of the paint, e.g. the binder.

## **Data Treatment**

PIXE spectra have been fitted by GUPIX or GUPIXWIN<sup>16</sup>, which extract elemental concentrations of the mineral compounds. BS spectra are simulated with SIMNRA<sup>17</sup> for both parts of the spectra RBS and BS. Automated PIXE-RBS depth profiling using PIXE spectra and RBS<sup>18,19</sup> is in progress.

## **Damage**

Particle interaction with paint matter can induce the appearance of dark brownish stains<sup>20</sup>, which are generally attributed to the formation of color centers<sup>21,22</sup>. The proton energy loss being less than the helium ion energy loss, damages induced by proton could be less significant. Furthermore, PIXE and BS were performed simultaneously, limiting the experiment time, interactions and consequently, the potential discoloration of the pigment.

## **RESULTS**

### **Elemental Composition of Mineral Compounds by PIXE**

Matrix composition has been calculated from the low-energy X-ray spectrum. The matrix composition gives access to the pigment identification. In case of extender, which can be added to the pigment in order to thicken the paint or to reduce the amount of the costly pigments, PIXE is very useful to determine the proportion of extender in the mixture. Trace elements can be extracted from the high-energy X-ray spectrum. Heavy elements of the matrix were also confirmed. Elements identifying lead white (Pb or S, Pb according to the sample), basic lead sulphate (S, Pb), calcium sulphate (S, Ca), gypsum (S, Ca), calcite (Ca), zinc oxide (Zn), titanium oxide (Ti) have been detected either in the pure pigment pellets as well as in the paint layers. It is noticeable that the term "lead white" is used for either lead carbonate or lead sulphate. Linseed oil has not been detected with PIXE. Due to our calculation procedure that normalizes the concentrations to 100 % total, the organic part of the paint has not been taken into account.

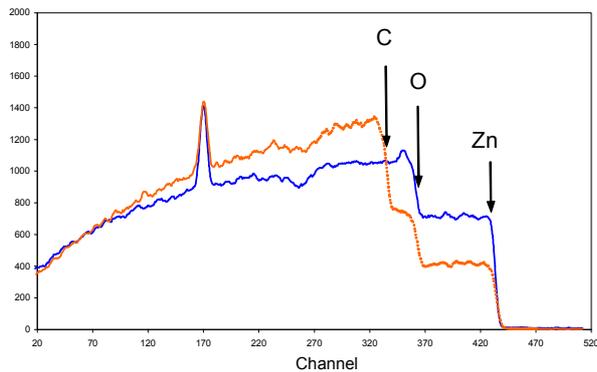
### **Organic Compounds and Depth Resolution by BS**

#### *Binder Estimation*

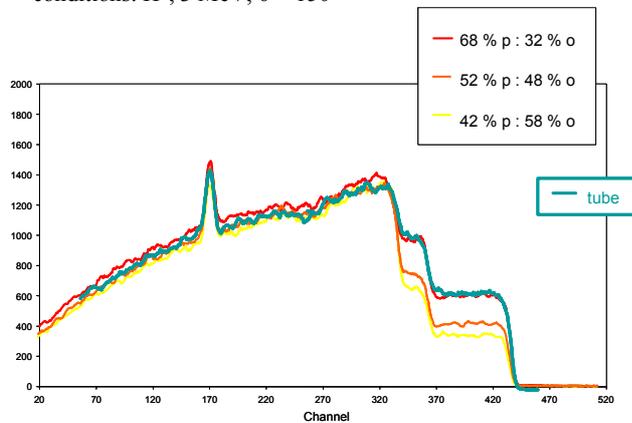
Figure 1 shows the comparison between pure pigment and paint. The pigment spectrum is characterized by two edges corresponding to the backscattered ions on zinc and oxygen. The intensity of the plateaus leads to the 1:1 stoichiometry of ZnO. The paint spectrum shows the same features with in addition the C signal from the linseed oil. Figure 2 compares various amounts of oil and pigment to a commercial paint.

**TABLE 1.** Advantages and limitations of 3 MeV protons for painting analysis

	Routine conditions	Selected conditions for paintings	Advantages	Limits
PIXE	2-3 MeV protons	3 MeV protons	Intense cross sections	Low-Z elements ( $Z < 11$ ) not detected. No information on organic compounds
RBS	2-3 MeV helium ions		Non-Rutherford cross sections for light elements (improvement of C and O detection) Large analyzed depth	Low selectivity
PIGE	3 MeV protons		Intense cross section for Na	Low cross sections for high-Z elements



**FIGURE 1.** BS spectra of the white pigment ZnO. Comparison between pure pigment (blue line) and mixture of pigment and linseed oil (dotted orange line). Experimental conditions:  $H^+$ , 3 MeV,  $\theta = 150^\circ$



**FIGURE 2.** BS spectra of various thick samples of ZnO paints. Comparison between three mixtures of pigment (p) and linseed oil (o) (red-orange-yellow lines) and a commercial paint (green line). Experimental conditions:  $H^+$ , 3 MeV,  $\theta = 150^\circ$

By comparison with the test samples or by calculation, the result gives a mixture of about 70 % pigment-30 % oil for the commercial paint tube. BS is not able to identify the nature of the organic compounds but thanks to the intensity of the C signal, it is possible to estimate its amount.

### Paint Layer Thickness

Lead white layers (in this study, basic lead sulphate on gypsum) have been investigated by simultaneous PIXE and BS. Layer thickness has been calculated from the SIMNRA simulation or from the surface energy approximation<sup>23</sup>, which uses the low energy edge of the Pb signal (Figure 3). Results are summarized in Table 2. The atom concentrations in Pb, O and C have been calculated by using the SIMNRA code. The proportion of pigment and linseed oil have been deduced by converting the atomic concentrations into weight percentages giving 74.5 % lead white and 25.5 % oil. These results are in close agreement with the expected values chosen by the painter: 76/24 ratio, which seems to be the optimal conditions for a good paint preparation.

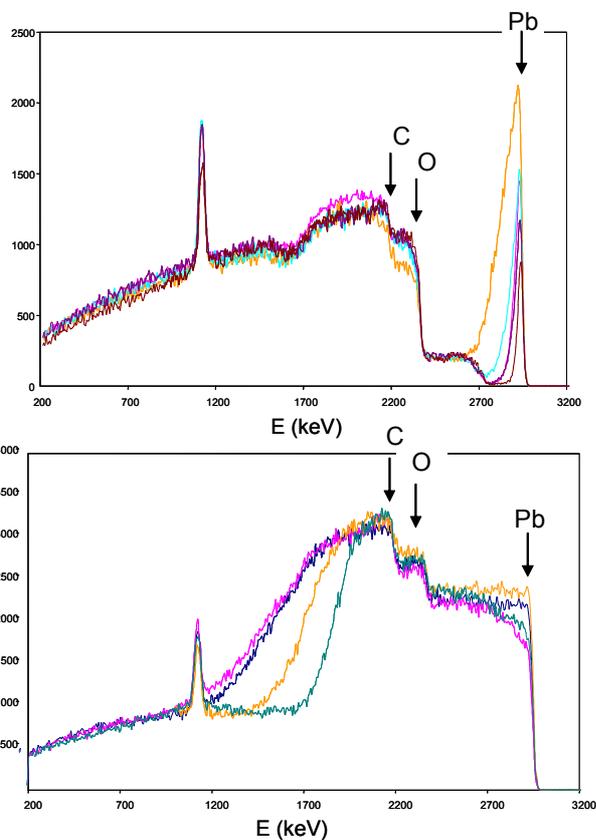
### Varnish Layer Thickness

The combination of PIXE and BS can give access to the analysis of a paint layer under varnish. The identification of the elements of the paint layer has been determined by the X-ray spectrum which has not been modified (in energy) by the varnish layer. On the other hand, due the proton energy loss through the varnish, the energy of the backscattered protons by the atoms of the paint layer has been shifted to the low energy side (Figure 4). This shift has been used to calculate the varnish thickness ( $\approx 1 \mu\text{m}$ ).

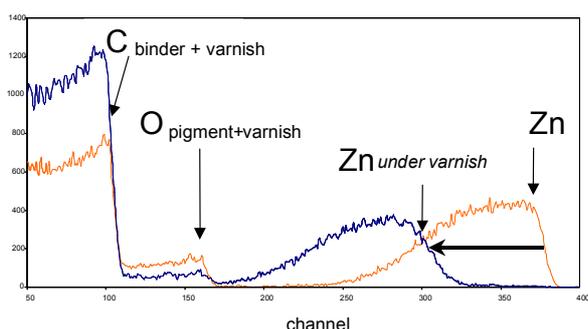
## CONCLUSION

The combination of PIXE and BS is useful 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 brings the thickness information and the organic compound estimation. The simultaneous PIXE and BS experiments get the advantages of analyzing the same area in one experiment. The experimental

time (about 10 minutes by point) is short, restraining beam damages. The data treatment is handy by using routine available simulation softwares.



**FIGURE 3.** BS spectra of series of thin (above, sample n°1) and thick (below, sample n°2) lead white paint layers on gypsum. Pb and O come from the pigment and C from the linseed oil. Experimental conditions:  $H^+$ , 3 MeV,  $\theta = 150^\circ$



**FIGURE 4.** Comparison of BS spectra of a paint layer of ZnO (orange line) and the same layer covered by a layer of varnish (blue line). Experimental conditions:  $He^{2+}$ , 5 MeV.

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**TABLE 2.** Lead white layer thickness ( $\mu\text{m}$ ) measured by Scanning Electron Microscopy (SEM), X-ray fluorescence (XRF) and BS

Sample	SEM	XRF	BS
1	0-13	4	1-4
2	15-38	17	25-32
3	48-71	89	> 40

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